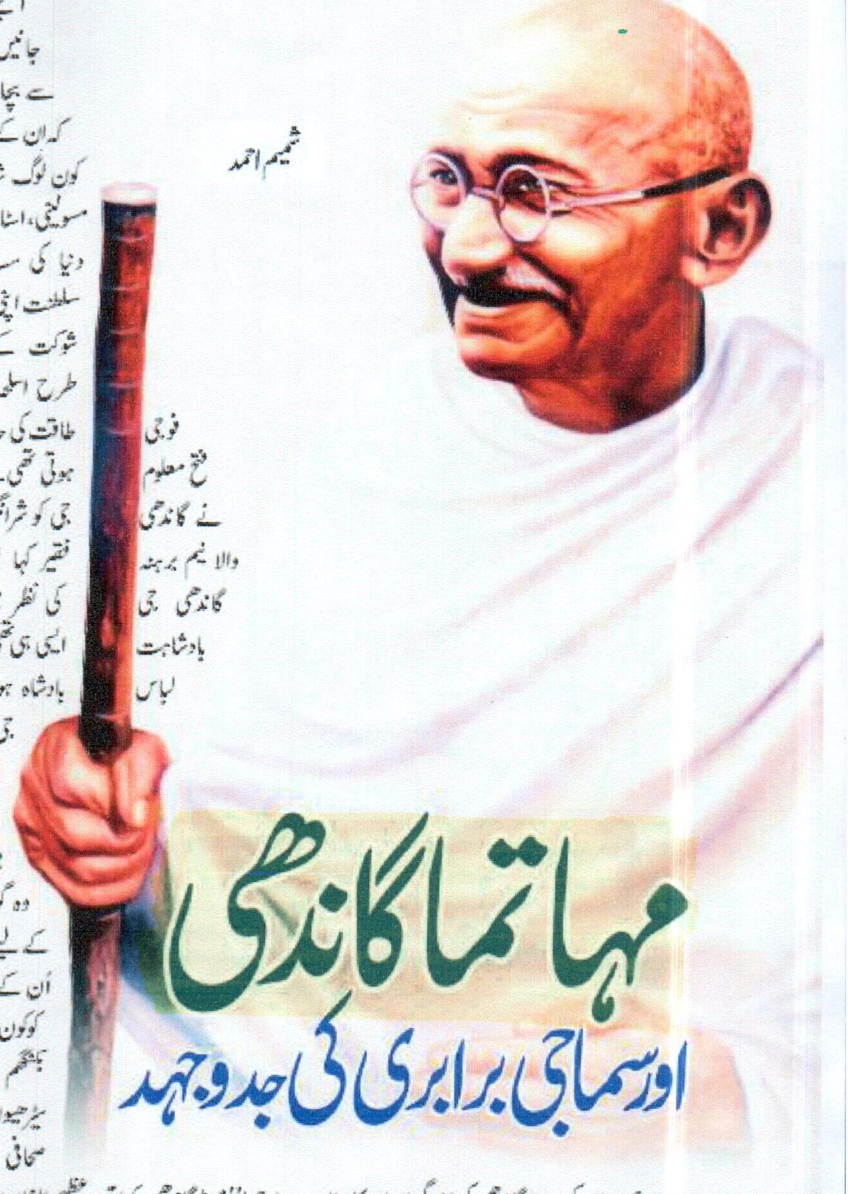

مہاتما گاندھی اور سماجی برابری کی جدوجہد

شمیم احمد

موہن داس کرم چند گاندھی کی زندگی اور ان کا پیغام برصغیر کی روح میں اسی طرح رواں دواں ہے جیسے مقدس دریائے گنگا رواں ہے۔ ان کے تصورات اور سرگرمیوں نے کبھی نہ منقسم ہونے والی ہماری لہروں کی طرح کئی افراد اور جمعیتوں کو متاثر کیا ہے۔ ہماری معاصر دُنیا میں کوئی شخص کس طرح اس انتہائی غیر معمولی روشنی کا صحیح احساس کرسکتا ہے جس نے دنیا بھر کو منور کیا۔ ایک ایسی شمع جس نے منکسر المزاجی کو فروغ دیا اور دُنیا کے روشن ترین شہروں میں جگمگائی؟ یہ پیار، اُمید اور امن کی شمع تھی۔

گاندھی جی کی شخصیت بیسویں صدی کا حقیقی معجزہ تھی۔ ایک ایسی صدی جس کے ابتدائی پچاس سالوں میں سات کروڑ سے زیادہ لوگوں کی جانیں تلف ہوئیں اور شاید یہ کہ گاندھی نے اپنی روحانی طاقت کے استحکام سے اکیلے ہی مزید جانیں ضائع ہونے سے بچالیں۔ غور کیجیے کہ ان کے معاصرین میں کون لوگ شامل تھے، ہٹلر، مسولینی، اسٹالین، اور ماؤ اور دنیا کی سب سے طاقتور سلطنت اپنی تمام تر شان و شوکت کے ساتھ پوری طرح اسلحہ سے لیس اور فوجی طاقت کی حامل، جو ناقابل فتح معلوم ہوتی تھی۔ ونسٹن چرچل نے گاندھی جی کو شرانگیزی پھیلانے والا نیم برہنہ فقیر کہا تھا۔ جب کہ گاندھی جی کی نظر میں چرچل کی بادشاہت ایسی ہی تھی جیسے کوئی بے لباس بادشاہ ہو۔ لیکن گاندھی جی نے اسے اتنی ناشائستگی سے ادا نہیں کیا۔ 1932 میں جب وہ گول میز کانفرنس کے لیے لندن میں تھے اُن کے اُس مشہور تبصرہ کو کون بھول سکتا ہے؟ بکنگھم پیلیس کی سیڑھیوں پر ایک انگریز صحافی نے اُن سے پوچھا ''مسٹر گاندھی، کیا آپ عظیم الشان سلطنت کے عظیم بادشاہ سے ملنے کے لیے ایک ادھ ننگے فقیر کی صورت میں جارہے ہیں؟''

گاندھی جی نے جواب دیا ''میرے دوست تم گھبراؤ نہیں حکمراں بادشاہ اتنے کپڑے پہنے ہوگا کہ وہ ہم دونوں کے لیے کافی ہوں گے۔''

موہن داس کرم چند گاندھی ہم میں سے زیادہ تر کی طرح ایک عام سے طالب علم تھے۔ وہ ایک شرمیلے اور منکسر المزاج وکیل بن گئے۔ اپنے اہل خاندان کی مدد کے لیے انہوں نے جنوبی افریقہ میں چھوٹے ہندوستانی تاجروں، مشروط مزدوروں اور وہاں کی افریقی آبادی کے درمیان وکالت کرنے کا فیصلہ کیا۔ 23 سال کی عمر میں، جب انھیں ناٹل میں ایک چھوٹا کیس ملا تو وہ بذریعہ جہاز بمبئی سے ڈربن کے لیے روانہ ہوگئے۔ وہ وہاں مختصر مدت کے لیے گئے تھے لیکن تقریباً 21 برس رہے۔ انھوں نے انگریزی حکومت کی تاریخ بدل ڈالی اور دنیا میں ہر جگہ کے مرد و زن کو سیاسی آزادی سے بڑھ کر سماجی برابری کی جدوجہد کی تحریک دی۔

گاندھی جی نے اختیار سے محروم لوگوں کو با اختیار بنایا کیونکہ وہ جانتے تھے کہ انسانی روح خدا کا عطا کردہ سب سے قوی تحفہ ہے۔ شاید انسانی تاریخ میں سب سے بڑھ کر انھوں نے انسانی روح کی قوت کو سمجھا۔ ایک ایٹم میں چھپی طاقت کی طرح، انھیں روح کی لافانی طاقت کا اندازہ ہوگیا تھا۔ جو اپنی تمام تابانی کے ساتھ رہا ہونے کی منتظر ہے۔

انھیں یہ غیر معمولی تصورات اپنے مطالعے سے ملے۔ وہ گہری تخلیقیت کے ساتھ مطالعہ کرتے تھے۔ کوئی انسانی فکر اُن کے لیے اجنبی نہیں تھی۔ صرف 19 سال کی عمر میں جب وہ لندن میں تھے انھوں نے مغربی کلچر کے عظیم ادیبوں، رسکن، ٹالسٹائی اور تھورو کا مطالعہ کرلیا تھا۔ لندن میں اُن کے قیام نے ہندوستانی تمدن پر کتابوں کے مطالعہ نے اُن کے طبعی میلان کو اور ہوا دی۔ انھوں نے سب سے پہلے بھگوت گیتا کا انگریزی ترجمہ پڑھا۔ ان کی والدہ، ان کا ماحول اور بچپن کے کچھ دوستوں کی صحبت سے اُن کے جوان احساسات کی تربیت ہو ہی چکی تھی۔ حضرت عیسیٰ کے مشہور زمانہ پہاڑی وعظ اور لاطینی، یونانی نیز انگریزی کی کتابوں نے ان کی بالغ فکر کی تشکیل کی۔

23 برس کی عمر میں ایک نوجوان وکیل کے طور پر جب وہ جنوبی افریقہ گئے تو اُن کی یہ روشن خیالی سب سے زیادہ قابل حصول قوت حیات بن گئی۔ ہر نسل و ذات کے لوگ اُن کے دوست بن گئے، یہودی، عیسائی، مسلمان، پارسی، ہندو- اُمرا اور مزدور، مبلغین و اساتذہ، سیاستداں و دانشور، کلرک اور مذہبی رہنما۔ انھوں نے کہا، اور زور دے کر کہا کہ اگر تم انصاف چاہتے ہو تو دوسروں کے ساتھ انصاف کرو۔ اُن کی دنیا میں کسی کے اخراج کا کوئی جواز نہیں تھا۔ زندگی سب کی شمولیت کا نام ہے۔

یہ سب اس وجہ سے ہوا کہ 7 جون 1893 کی ایک سرد رات میں انھیں ریل گاڑی کے فرسٹ کلاس کے ڈبے سے اس وقت باہر نکال دیا گیا جب وہ وکیلوں کے خوش وضع لباس میں ڈربن سے پریٹوریا جارہے تھے۔ وہ گارڈ جس نے انھیں انتہائی غیر مہذب طریقے سے نکال باہر کیا شاید ہی اپنے بے سوچے سمجھے اور سخت گیر رویے کے اتنے غیر معمولی اور دور رس نتائج کا اندازہ کرسکا ہوگا۔ اگلے پچاس سال کے اندر عظیم الشان سلطنت ٹوٹ

کلامِ اقبال میں شمشیر وسناں کی ایمائی کیفیات

ڈاکٹر شمیم احمد

سینٹ اسٹیفنز کالج، دہلی یونیورسٹی، دہلی، موبائل: 9811320531

ممولے کو شہباز سے لڑا دینے کا پیغام دینے والے، دہقان کو روزی بہم نہ پہنچانے والے کھیت کے ہر خوشۂ گندم کو جلانے کا حکم دینے والے، خودی میں ڈوب کے ضربِ کلیم پیدا کرنے کی راہ دکھانے والے اقبال کے کلام میں جنگ وجدال، تیغ وتفنگ اور شمشیر وسناں کے لفظی ومعنوی پیکر جگہ جگہ اپنی بہار دکھاتے ہیں۔ لہو گرم رکھنے کے ایک بہانے کے طور پر جھپٹنے، پلٹنے اور پلٹ کر جھپٹنے کی صفت رکھنے والے شاہین سے اقبال کو اسی لیے خصوصی شغف ہے۔ انھیں اس بات پر فخر ہے کہ شاہین کی طرح ان کا کلام بھی بادِ بہاری، گلچیں، بُلبُل اور عاشقانہ نغموں کی بیماری سے پاک ہے۔ وہ خونِ دل وجگر کو سرمایۂ حیات سمجھتے ہیں۔ ان کے نزدیک انسان کی فطرت جل ترنگ نہیں لہو ترنگ ہے۔ بالِ جبریل میں اپنے کلام کی اسی ہنگامہ خیزی پر فخر کرتے ہوئے کہا ہے:

یوں دادِ سخن مجھ کو دیتے ہیں عراق و پارس
یہ کافرِ ہندی ہے بے تیغ و سناں خوں ریز

قلم کی نوک سے تلوار کی دھار کا کام لینے والے اقبال یہ اعلان بھی کرتے ہیں کہ بے نیام تلوار کی کیفیت انھوں نے کس طرح اختیار کی ہے:

ذرا تقدیر کی گہرائیوں میں ڈوب جا تو بھی
کہ اس جنگاہ سے میں بن کے تیغِ بے نیام آیا

گویا تقدیر کی گہرائی دراصل کوئی میدانِ جنگ ہے جس میں ڈوب کر وہ اسرار عیاں ہوتے ہیں جو انسان کے جرأت وحوصلے کی افزونی کا باعث بنتے ہیں۔ اپنی رضا کے مطابق اپنی تقدیر خود تحریر کرانے کا حوصلہ صرف انھی لوگوں میں پیدا ہوتا ہے جو اپنی خودی کو پختہ تر کرنے کے لیے کوشاں رہتے ہیں۔ اقبال کو اس پر ناز ہے کہ نکتہ ہائے خودی کے جو حوالے ان کے کلام میں جگہ جگہ ملتے ہیں وہ دراصل تلوار کی مانند ہیں اور اگر کوئی شخص ایسی بصیرت کا حامل نہیں کہ ان نکات کی تفہیم کر سکے تو بہتر یہ ہے کہ وہ کلامِ اقبال کی طرف التفات نہ کرے۔

نظر نہیں تو مرے حلقۂ سخن میں نہ بیٹھ
کہ نکتہ ہائے خودی ہیں مثالِ تیغِ اصیل

بالِ جبریل کی اسی غزل میں شہادت وقربانی کے پردے میں تاریخ اسلام کے دو مابہ الامتیاز واقعات کو داستانِ حرم کی ابتدا اور انتہا کے ایک دھاگے میں پرو کر شہادتِ حسینؓ کے بیان کو نئی عظمتوں سے ہم کنار کیا ہے:

غریب و سادہ و رنگیں ہے داستانِ حرم
نہایت اس کی حسینؓ، ابتدا ہے اسمٰعیلؑ

انسانی تہذیب وتمدن کی بنیاد جن اصولوں پر قائم ہے ان میں سب سے اہم جان کا تحفظ ہے۔ جس معاشرے میں انسانی جان اور خون کا احترام نہیں کیا جاتا اس معاشرے کو دنیا ناپسندیدگی کی نگاہ سے دیکھتی ہے۔ انسان کے تمدنی حقوق میں اولین حق زندہ رہنے کا حق ہے اور اس کے تمدنی فرائض میں اولین فرض زندہ رہنے دینے کا فرض ہے، لیکن اگر کوئی شخص یا حکومت زندہ رہنے دینے کے اپنے فرض سے چشم پوشی کرے اور اپنی انا کی تسکین کی خاطر یا اپنے مفادات کی تکمیل کی غرض سے انسانی جان کی قاتل بن جائے تو پھر ایسے اشخاص کی سرکوبی ضروری ہے۔ زندہ رہنے کا حق صرف جائز حدود کے اندر ہی دیا جا سکتا ہے۔ جب کوئی شخص ان حدود سے تجاوز کر کے فتنہ وفساد پھیلائے یا دوسروں کی جان پر ناحق حملہ کرے تو وہ خود بخود اپنے حق زندگی کو کھو دیتا ہے۔ اس کے خون کی حرمت زائل ہو جاتی ہے اور پھر اس کی موت ہی انسانیت کی حیات ہوتی ہے۔ قتل وہلاکت خیزی بڑی بُری چیز ہے مگر اس سے زیادہ خراب چیز فتنہ وفساد ہے۔ جب کوئی شخص اس بُرے جرم کا مرتکب ہو تو اس بڑی برائی کا خاتمہ کر دینا ہی زیادہ بہتر ہے۔

کلامِ اقبال میں شمشیر بہ کف ہونے اور جنگ وخوں ریزی کی طرف قدم بڑھانے کا تمام تر پیغام صرف اسی لیے ہے کہ مظلوم کی حمایت کی جائے۔ اس کے سلب شدہ حقوق اسے دلائے جائیں۔ جس ظالم نے انسانوں پر عرصۂ حیات کو تنگ کر دیا ہے اس کو جینے کا حق حاصل نہیں۔ فتنہ گر کو شکست دینے کے لیے تلوار اٹھانا ضروری ہے۔ انسانوں سے سچی محبت کرنے والا انسان اپنے جیسے کسی دوسرے انسان کو ظلم وزیادتی کا شکار ہوتے ہوئے نہیں دیکھ سکتا۔ انسانی تاریخ بتاتی ہے کہ نیک انسانوں نے ہمیشہ ظالم کو کیفرِ کردار تک پہنچانے کے لیے تلوار اٹھائی ہے۔ محبت اور پاکیزگی کے پیکر 'رام' میں بھی اقبال کو یہ خوبی نظر آئی کہ راون کے خاتمے کے لیے سری رام نے بڑی جرأت، حوصلے اور ہنرمندی کا ثبوت دیا۔

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अकथितं चेति सूत्रार्थविचार

Abhay Singh

प्रस्तावना

वेदाङ्गेषु प्रमुखं व्याकरणम्। मुखं व्याकरणं स्मृतमिति भाष्योक्तिः[1]। मुखमिव प्रधानत्वात् मुख्यः प्रथम इत्यर्थः। छान्दसं व्याकरणं, लौकिकं व्याकरणम्, छान्दसलौकिकं व्याकरणमित्येवं व्याकरणस्य भेदत्रयम्। कानिचन लौकिकशब्दानामेव व्युत्पादकानि, कानिचित् वैदिकानामेव व्युत्पादकानि। पाणिनीयव्याकरणं तु उभयव्युत्पादकतया छान्दसलौकिकमित्युच्यते। सत्स्वपि बहुषु व्याकरणेषु पाणिनीयमेव भजते लोकः। व्याकरणस्यास्य प्रक्रियाप्रस्थानम्, आर्थिकप्रस्थानमिति द्वयी गतिः। प्रकृतिप्रत्ययविभागद्वारा शब्दसंस्कारमाद्यम्। प्रकृतिप्रत्ययचिन्तनमेव आर्थिकप्रस्थानमित्युच्यते। आर्थिकप्रकरणे च विभक्त्यर्थविचारः सर्वातिशायी दृश्यते। तत्र हि—

कर्ता कर्म च करणं सम्प्रदानं तथैव च।
अपादानाधिकरणे इत्याहुः कारकाणि षट्।।

इत्युक्तरीत्या षट् कारकाणि प्रतिपादितानि। तत्र द्वितीयाविभक्तिप्रयोजककर्मसंज्ञाविधायकानि नव सूत्राणि दृश्यन्ते कारकप्रकरणे—

- कर्तुरीप्सिततमं कर्म[2]
- तथायुक्तं चानीप्सितम्[3]
- अकथितं च[4]
- गतिबुद्धिप्रत्यवसानार्थशब्दकर्माकर्मकाणामणि कर्ता स णौ[5]
- हृक्रोरन्यतरस्याम्[6]
- क्रुधद्रुहोरुपसृष्टयोः कर्म[7]
- अधिशीङ्स्थासां कर्म[8]
- अभिनिविशश्च[9]
- उपान्वध्याङ्वसः[10]

तत्र क्रुधद्रुहेर्ष्यासूयार्थानां यं प्रति कोपः इति सूत्रेण प्राप्तस्य सम्प्रदानस्य कर्मसंज्ञाविधायकं क्रुधद्रुहोरुपसृष्टयोः कर्म इति सूत्रम्। अधिशीङ्स्थासां कर्म,अभिनिविशश्च, उपान्वध्याङ्वसः इतीमानि सूत्राणि आधारस्य कर्मसंज्ञां विदधते। गतिबुद्धिप्रत्यवसानार्थशब्दकर्माकर्मकाणामणि कर्ता स णौ, हृक्रोरन्यतरस्याम् इति सूत्रे द्वे अण्यन्तावस्थायां कर्तुः ण्यन्तावस्थायां कर्मत्वं विदधाते।

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[1] महाभाष्य पस्पशाह्निकम् पृ. 10
[2] अष्टाध्यायी 1.4.49
[3] अष्टाध्यायी 1.4.50
[4] अष्टाध्यायी 1.4.51
[5] अष्टाध्यायी 1.4.52
[6] अष्टाध्यायी 1.4.53
[7] अष्टाध्यायी 1.4.38
[8] अष्टाध्यायी 1.4.46
[9] अष्टाध्यायी 1.4.47
[10] अष्टाध्यायी 1.4.48

The Chinese Puzzle

Pallavi Aiyar, *Smoke and Mirrors: An Experience of China* (New Delhi: Fourth Estate, 2008),
pp. 273, Paperback, Rs.450

Aditya Pratap Deo
St Stephen's College

Written in 2008, Pallavi Aiyar's *Smoke and Mirrors: An Experience of China* remains as relevant today as then, even though the pace of change in China has been unusually rapid. Written like an extended diary, reflections on her 5-year stint in China from 2002 onward (working as an English language instructor first, and then journalist), Aiyar's book is at a deeper level a document about the human condition in one of humankind's greatest revolutions – the transformation of China in our time. But the book is also as much about India as it is about China, two peoples joined by geography, history and culture, but also, from the Indian side, anxiety about its resurgent neighbor. Aiyar writes for an India unable to fully grasp what is happening in China, sometimes comparing the two, at other times, more directly if also a little simplistically asking: what could India learn from China? (p. 239). For someone who has just returned from a trip to China, many years after Aiyar lived there, I believe that in many ways the questions are still the same except that the lag on the Indian side has become more comprehensive, acute and exasperating. Here, I will not dwell on Indian anxieties about China. We live it all the time. My focus, as a historian, will be to read *Smoke and Mirrors* as a document of history, a kind of ethnographic history of the everyday in fast-changing China, where the author, in her perceptive, sensitive and evocative prose, weaves a picture of a society in transition. Her wit and humor add an aspect of irony to her prose that is remarkable.

The first chapter (pp. 10-27) – *Better Fat than Anapple* – deals with Aiyar's introduction to China, primarily through her interaction with her students at the Beijing Broadcasting Institute, where she first comes face to face with the puzzle that is China. Writes Aiyar: 'The China I lived in was a communist country in name but a strange hybrid in practice…students sat through compulsory classes in Marxism and Maoist thought, bored blind, fantasizing of little but money' (pp.15-16). Her struggle with the language, amusement at finding that young people learning English invariable take funny English names, realization of how deep they had been socialized into being apolitical, and (almost) horror at discovering the women students' bizarre fixation with large eyes, among other things, give us a sense of how strange and mixed-up a place China appears at first glance.

From her work place, Aiyar eases us out into the streets of Beijing, the city which was to be her home in China, a city in the grip of a huge make-over for the Olympics in 2008, a prestige event that the Chinese government, already in the midst of supervising the massive transformation of its cities, was bent upon making a success at all costs. This chapter – *Olympian Makeover* (pp. 28-50) – tracks the demolition of a very large part of historic Beijing, 25 million square meters, and the creation of a swanky new city with a Central Business District, 'the capitalist core of the communist capital' (p. 28). According to Aiyar, 'the pace of the current transformation was unbeatable as was its reach, as it pushed into every nook and corner, bulldozing its way into even Mongol-period enclaves that had so far miraculously remained intact' (p. 37). In this city in the throes of an 'identity crisis' (p. 36), the Chinese people, observes Aiyar, used to the 'ceaseless impermanence' and 'flux (p. 39)' of their recent past, showed a certain 'equanimity' that 'would have made the Buddha proud' (Ibid.).

In the next chapter, titled *Coronavirus* (pp. 51-70), the writer comes to grips with the Chinese government's obstinate refusal, shored up through censorship and socialization, to first recognize the SARS epidemic, then its volte-face in the face of aggravated circumstances, and the subsequent scramble for damage control. Stunned, Aiyar

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Enhanced dielectric properties of $Ba_3ZnTa_{2-x}Nb_xO_9$ in microwave region using tungstic acid

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ABSTRACT

Dielectric resonators belonging to the families of complex perovskite $Ba_3ZnTa_{2-x}Nb_xO_9$ were synthesized by a solid-state reaction route. Calcination at 1250°C leads to oxides with ordered (hexagonal) perovskite structure over the range ($0.25 \leq x \leq 1.75$). However, ordering refraction intensity of PXRD patterns increased on sintering at 1340°C with tungstic acid, as a sintering aid. Sintering has lead to >90% density. In microwave range, $Ba_3ZnTa_{0.5}Nb_{1.5}O_9$ shows much higher permittivity (35) and quality factor (43,120 GHz).

ARTICLE HISTORY
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KEYWORDS
Perovskite; 1:2 ordering; dielectric properties; high *Q*; ceramics

1 . Introduction

For more than two decades, the perovskite-based dielectric resonator had emerged as a promising material because of the combination of high relative permittivity ($\varepsilon_r > 25$), high Q ($Q = 1/\tan \delta > 5000$) and low temperature coefficient of resonant frequency ($\tau_f \sim 0$ ppm/°C) and hence found widespread applications as filters and oscillators [1]. The microwave communication had revolutionized the wireless communication that depends on the dielectric resonators with superior properties. The perovskite based on $Ba(Zn_{1/3}Ta_{2/3})O_3$ had been widely used as a dielectric resonator material and this gave the material research a new direction and led to the discovery of several new compounds by appropriate substitutions at Zn and Ta sites.

Galasso et al. reported that $Ba(Zn_{1/3}Ta_{2/3})O_3$ can crystallize in 1:2 ordered structure [2,3] and these results were further confirmed by Endo et al. [4], Kawashima et al. [5]. $Ba(Zn_{1/3}Ta_{2/3})O_3$ has disordered structure at lower temperature, which transforms into ordered form (hexagonal structure) at temperatures around 1400°C and is being used commercially in various devices [5]. During the transition from disordered to ordered state, the symmetry change from Pm3m to P3m1, the ordering and disordering depend on the diffusion of cations. Heat treatment is one of the main factors in controlling order–disordered phase formation. The Niobium analogue, $Ba(Zn_{1/3}Nb_{2/3})O_3$ can also crystallize in 1:2 ordering [6]. $Ba(Zn_{1/3}Nb_{2/3})O_3$ was reported to have disordered structure till the studies done by M. A. Akbas et al. in 1998 where they reported that with proper annealing at 1400°C for 12 h, ordered perovskite structure can be obtained [7]. Quenching or annealing at a temperature higher than this can lead to disordered structure attributing to the formation of liquid phase at grain boundaries [6,7]. The increase in the amount of liquid phase and subsequent lattice imperfections at high temperature leads to decrease in ordering. The 1:2 ordering is very vital for the high Q values. The volatile nature of Zn adds to the problem. The longer sintering and annealing time required for improvement in degree of ordering leads to evaporation of Zinc from the ceramic making the surface rich on barium niobate [8].

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Microwave dielectric properties of (1-x)$Ba(Mg_{1/3}Ta_{2/3})O_3$ – (x)$Ba(Mg_{1/8}Ta_{3/4})O_3$ ceramics synthesized by one pot metathesis process

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ABSTRACT

Complex perovskites (1-x)$Ba(Mg_{1/3}Ta_{2/3})O_3$ – (x)$Ba(Mg_{1/8}Ta_{3/4})O_3$ ($0 \leq x \leq 1$) were investigated for possible solid solution and composite range using one pot metathesis process. This process lowers the synthesis temperature of Ba-Mg-Ta ceramics to just 1100 °C. Till $x = 0.5$ the powder X-ray pattern shows the presence of only $Ba(Mg_{1/3}Ta_{2/3})O_3$ phase. Above $x = 0.5$ both $Ba(Mg_{1/3}Ta_{2/3})O_3$ and $Ba(Mg_{1/8}Ta_{3/4})O_3$ phase starts crystallizing. The samples can be sintered to >90% density at around 1350 °C. Dielectric properties measured at GHz frequency exhibits values in the range: $\varepsilon_r = 22 - 29$, Q.f = 7000 – 36000 GHz and $\tau_f = 14 - 50$ ppm/°C.

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KEYWORDS
One pot metathesis process; dielectric properties; $Ba(Mg_{1/8}Ta_{3/4})O_3$; $Ba(Mg_{1/3}Ta_{2/3})O_3$

1. Introduction

Complex perovskites ceramics with general formula $A(M_{1/3}M'_{2/3})O_3$ where $A = Ba^{2+}$, Sr^{2+}, $M = Mg^{2+}$, Zn^{2+}, Ni^{2+}, Co^{2+} and $M' = Nb^{5+}$, Ta^{5+} show excellent dielectric properties and hence used as dielectric resonators at microwave frequencies [1–3]. In comparison to niobates, tantalates show relatively high quality factor (low loss), therefore they have high commercial value. Apart from high quality factor or low loss, good dielectric resonator should also have high permittivity value (ε_r) and almost zero temperature coefficient of resonant frequency (τ_f). $Ba(Mg_{1/3}Ta_{2/3})O_3$ is one such commercially valuable tantalates which exhibits highest quality factor (Q.f > 3,00,000 GHz), permittivity ($\varepsilon_r \sim 25$) and very low temperature coefficient of resonant frequency ($\tau_f <$ 4 ppm/°C) among its other analog [4–11] but these properties are normally observed after sintering at extremely high temperatures (>1600 °C) [5, 7, 9, 10, 12] with long soaking time (>100 hours) [11, 13]. Researchers have tried different methods of synthesis [14–16] and different dopants [17, 18] to improve its dielectric properties and lower down its synthesis temperature, but they normally ended up with some secondary phase or degraded properties. Reproducibility is also a matter of concern for $Ba(Mg_{1/3}Ta_{2/3})O_3$, as its properties and structures get highly influenced by synthesis method. One pot metathesis process is a variation of molten salt synthesis. It is based on metathetical

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Biochemical synthesis of coumarin glycosides: A review†

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Coumarin glycosides have shown immense potential for diverse biological activities and have been explored extensively as highly prospective biomolecules. In recent years, coumarin glycosides have been used as enzyme inhibitor molecules, environmentally-sensitive fluorescent sensors, the building material of single-excitation and dual emission graphene composite, fluorophore-tagged glycosides, molecule to assay enzyme activity on model bacterial strains, the nucleoside monomer unit for the photoswitchable formation of a DNA interstrand cross-link along with many other applications. In this review, we have compiled biochemically afforded coumarin glycosides obtained *via* mutagenic synthesis, chemo-enzymatic synthesis and hairy root culture system synthesis. This review will play the role of a reservoir of biochemically synthesized glycosylated coumarins and encourage medicinal chemists to explore the potential of these molecules as drug candidates and further biological applications.

Keywords: Coumarins, coumarin glycosides, mutagenic synthesis, chemoenzymatic synthesis.

1. Introduction

Coumarins are heterocycles consisting of fused benzene and α-pyrone rings, which form a very significant class of natural products. After its first isolation from tonka beans, more than thirteen hundred types of coumarins have been isolated and identified as secondary metabolites from bacteria, fungi and green plants[1,2]. These naturally occurring compounds had displayed a wide array of biological and pharmacological activities, which encouraged scientists to synthesize their analogues. With an aim to produce analogue series, divergence was introduced in the basic coumarin moiety by various substitutions in the aromatic ring and 3- and 4-positions of benzopyran ring of the coumarin. Nevertheless, structural biodiversity in coumarin glycosides arises from the attachment of the sugar moieties at specific positions of the aglycon core. When attached to the drug molecules, they manoeuvre their solubility, membrane transport, pharmacokinetics and pharmacodynamics[3]. When used as a drug molecule, these sugar modules contribute towards the molecular recognition of their cellular target and help the aglycon part to affix with DNA strand by anchoring with its major or minor groove[4]. Biological relevances of the coumarin glycosides have inspired biochemists and microbiologists to develop various chemical, chemoenzymatic, enzymatic and engineered biosynthesis methodologies to fabricate coumarin glycosides. However, exploration of literature conceded that review articles on naturally occurring or synthesized coumarins[5–9] are not so plentiful in literature and moreover, coumarin glycosides were recorded as an insignificant part therein. On the other hand, the use of whole-cell fermentation (wild type/mutant) or application of isolated and purified natural-product enzymes have been found to be advantageous in comparison to classical methods of total synthesis of natural products which are often lengthy and afford very poor overall yield. In the modern manufacturing methodologies of natural products, fermentation processes are used widely for the manufacturing of mass production of natural products, such as antibiotics, vitamins and other

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†Review.

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Chemo-enzymatic route to bridged homolyxofuranosyl-pyrimidines

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Regioselective monoacetylation
Novozyme®-435
Bridged homolyxofuranosyl nucleosides

ABSTRACT

Synthesis of 2′-*O*,5′-*C*-bridged-*β*-D-homolyxofuranosyl nucleosides U and T have been achieved starting from diacetone-D-glucose in overall yields 55.7 and 57.1%, respectively. Quantitative regioselective monoacetylation of the lone primary hydroxyl group in trihydroxy nucleoside intermediate, *i.e.* 3′-*O*-benzyl-*β*-D-glucofuranosyl nucleosides mediated by Novozyme®-435 has been utilized as the key step in the synthesis of homolyxofuranosyl nucleosides. The structure of the synthesized 2′-*O*,5′-*C*-bridged-*β*-D-homolyxofuranosyl uracil and -thymine has been established on the basis of their spectral (IR, ^{1}H, ^{13}C NMR and HRMS) data analysis and the structure of earlier nucleoside was confirmed by its X-rays diffraction analysis which revealed that these 2′-*O*,5′-*C*-bridged homo-nucleosides are locked into *S*-type sugar puckering.

1. Introduction

Modified nucleosides and their analogues are of much importance due to their immense potential as key precursors for the synthesis of oligonucleotide based therapeutic agents for RNA/gene targeting [1,2]. Most of the bicyclic sugar modified nucleosides possess constrained sugar puckering, which enable them to mimic a DNA or RNA type furanose ring conformation. The oligonucleotides derived from such nucleosides show high levels of complementarity with their corresponding DNA/RNA strands together with more stability towards nucleases. Quite a few sugar modified nucleosides have been found to exhibit excellent anti-tumour or antiviral activities [3].

Bicyclic nucleosides **1** and **2**, with extra methylene group in the sugar moiety are well known as locked nucleic acids (LNA) and used for the development of antisense/anti-gene oligonucleotides due to their restricted conformational structures (Fig. 1) [4–6].

Likewise, homonucleoside monomers having an additional methylene group at the C-5′ end as in nucleoside **3** [7–10] or between C-1′ and nucleobase as in nucleoside **4** [11,12] have established their significance with diverse biological activities. Extensive modifications have been carried out in the sugar ring to synthesize homonucleoside analogues, such as 1,3-dioxolane nucleosides **5** [13,14], homo-*N*,*O*-nucleosides **6** [15,16] and bicyclic-*N*,*O*-*iso*-homonucleosides **7** [17]. On the other hand, a 2′-*O*,5′-*C*-methylene-linked bicyclic nucleoside **8** was synthesized and its conformational studies revealed that it adopted *S*-type furanose configuration [18]. Two novel bicyclic nucleotide monomers **9** (5*R* & 5*S*) were synthesized with 3′-endo conformational restriction, where the sugar moiety had the D-arabinose conformation [19]. The 9-mer or 14-mer oligonucleotides with mono-, di- or tri-incorporation of these nucleoside monomers in oligonucleotides showed decrease in binding affinity towards complementary DNA and RNA. Variation of the heterocyclic rings and bicyclic structures associated with these homonucleoside analogues has enabled researchers to enhance the physiological/biological properties of oligonucleotides involving them. Further, potential activities of homocytidine **3a**, homouridine **3b** and homoarabinofuranosylcytosine **3c** have been evaluated against herpes simplex virus type 1 along with their cytoxicity against HL-60, K-562, U-937 and human LY-PHA cell lines (Fig. 1) [7]. Similarly, antiviral activity of oxazolidine homonucleosides **6** were examined against variety of DNA and RNA viruses and these nucleosides were found to be non-toxic up to 250 µM concentration [20].

We have reported the synthesis of several bicyclic and spiro-nucleosides where the bridging methylene group introduces conformational restriction to the sugar ring of the nucleoside [21–24]. Herein, we report a chemo-enzymatic synthesis of bicyclic 5′-homolyxofuranosyl nucleosides of U and T.

2. Results and discussion

It was envisioned that the targeted bridged homo-nucleosides would be synthesized from diacetone-D-glucofuranose because this is an orthogonally protected substrate that will provide tetraacetate intermediate for nucleobase coupling and subsequently produce our desired nucleoside monomer (Scheme 1).

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ORIGINAL ARTICLE

The direct synthesis of a substituted naphthopentathiepin for selective Co^{2+} ion recognition in aqueous solution

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Abstract

A new pentahiepin based on 1-naphthol unit was synthesized by direct condensation method, which on crystallization yielded triclinic crystals in the P-1 space group. The crystal structure was analyzed computationally through Gaussian and Crystal-Explorer software. An unusually high degree of short contacts originating from sulfur were observed. The intermolecular interaction investigations revealed that the sulfur atoms take a chair form suitable for metal coordination. Investigation of the affinity of the naphthopentathiepin towards metal ions revealed that the receptor forms a complex with Co^{2+} ions in 50% aqueous acetonitrile. By virtue of the cage type cavity offered by the pentathiepin derivative, it can form a complex with Co^{2+} ions in a sandwich fashion. The Job's plot confirmed 2:1 binding stoichiometry.

Keywords Cobalt sensor · Pentahiepin · Colorimetric sensor · DFT studies · TD-DFT studies · Crystal structure · X-ray analysis · Crystal explorer

Introduction

Supramolecular chemistry is an ever-expanding area for the development of sensors and switches for environmentally and biologically important heavy metal ions [1, 2]. Development of low cost, portable and easily available sensing device is tremendously important towards a sustainable solution for toxic ions [3]. Toxic analytes produced from the industrial sources entering into the ecosystem is a perennial threat. The development of innovative receptors with the aim of enhancing selectivity and their subsequent application in toxic metal ion recognition is of enormous interest these days [4]. Cobalt is a vital trace element in nutrition and its deficiency may lead to anemia, loss of appetite, vasodilation [5–7]. Varied disorders like allergy, nausea, gastrointestinal disorder are greatly prevalent owing to the cobalt ion poisoning [5–7]. Unregulated exposure of cobalt may also result in cardiac and thyroid enlargement, heart disease, and bone marrow malfunctions [8, 9]. Therefore, monitoring the distribution of cobalt ions in the environmental and biological system is essential. Hence, there is a strong need to detect a low level of cobalt ions for environmental remedies.

Although several techniques like inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), flame atomic absorption spectrometry are commonly employed to monitor cobalt ion concentrations in the samples collected from different sources [10–13]. However, long time scale, tedious sample preparation, expensive instruments create more hurdle in practical adoption of these techniques for monitoring the metal ion concentration in remote areas. Colorimetric detection of the analyte is easy to recognize and convenient method as a distinction can be achieved with naked eye evaluation [14].

Some of the reported sensors for Co^{2+} ions include substituted phenanthrolines [15], isothiazole [16], Schiff's base derivatives [17–19], mercapto compounds, Zn-terpyridine complex [20] etc. Sulfur is an important donor atom in supramolecular chemistry [21, 22]. Sulfur is widely used in medicines, bleaching of fabric, formulation of gun powder and vulcanization of latex [23]. Due to the inexpensive and

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chemosensors

Article

Colorimetric and Fluorescence-Based Detection of Mercuric Ion Using a Benzothiazolinic Spiropyran

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Abstract: A merocyanine dye as a *p*-toluenesulfonate salt was synthesized. The structure of the dye was characterized using IR, NMR, HR-MS and single crystal X-ray crystallography. The X-ray crystallographic studies revealed the formation of a stacked aggregated structure of the merocyanine dye. The stacking interactions were investigated using the Crystal Explorer program, which estimated the strength of the interactions between different molecular pairs. The merocyanine dye was screened for affinity towards heavy metal ions, which revealed a color change from pink to colorless in the presence of mercuric ions, while other metal ions did not produce a similar change in color. In addition, the fluorescence spectroscopy indicated a change in the fluorescence intensity upon addition of mercuric ions. Both techniques displayed a good limit of detection value towards mercuric ions. In addition, the pixel intensity-based detection technique was also employed for the determination of limit of detection value with the help of a smartphone. The dynamic light scattering (DLS) studies indicated that the optical change occurred in the spectra of the receptor is due to the disaggregation of the receptor induced by mercuric ions. In addition, ^{1}H-NMR studies were also used for investigating the mechanism of interaction between the receptor and the mercuric ions. The density functional theory (DFT) studies were used to investigate the formation of the complex at the molecular level, while time dependent density functional theory (TD-DFT) studies were used to understand the observed absorption spectra through the calculation of electronic excitation parameters, which indicated an increase in the energy difference between ground and the excited state.

Keywords: colorimetric sensor; optical sensor; mercury sensor; spiropyran; merocyanine form; reversible sensors; DFT; TD-DFT

1. Introduction

Mercury pollution is known to produce devastating effects on our environment [1,2]. Although mercury is present in the earth's crust, human activities are the biggest source of mercury in our environment [3–6]. Mercury pollution originates due to the release of mercury in our environment and water bodies from a variety of sources such as coal burning, chlor-alkali, cement, plastic, medical device, electrical, paper and certain pharmaceutical industries [7–9]. In particular, polluted water bodies can seriously affect the health of a population that depends on fish consumption for their survival [10]. Mercury exists in various forms: Elemental (or metallic), inorganic (to which people may be exposed through their occupation) and organic (e.g., methylmercury, to which people may be exposed through their diet) [11,12]. Once in the environment, mercury can be transformed by bacteria into methylmercury. Methylmercury then bio-accumulates in fish and shellfish, which occurs when an organism holds higher concentrations of the element than the surroundings [13,14]. People are mainly exposed to methylmercury, an organic compound when they eat fish and shellfish that contain the compound [15,16]. These forms of mercury differ in their degree of toxicity and in their effects on the nervous, digestive and immune systems, and on lungs, kidneys, skin, and eyes [17]. Exposure

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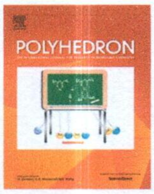

Synthesis and optical properties of copper(II) and nickel(II) complexes of a highly fluorescent morpholine-derivative

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Crystal structure
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ABSTRACT

A morpholine substituted methyl 3-hydroxy-2-naphthoate was synthesized. The morpholine derivative displayed an intense fluorescence. Owing to the presence of suitable donor atoms, it was employed for the detection of transition metal ions. The crystals of copper and nickel complexes of the fluorescence active ligand were grown via vapor diffusion method. The ligand structure and its metal complexes were characterized using ^{1}H NMR, IR, HR-MS and single crystal X-ray crystallography. The synthesized ligand displayed selective turn-off fluorescence response in the presence of Cu^{2+} and Ni^{2+} ions. Fluorescence active letters were encoded successfully on filter paper utilizing metal complexes as a tool towards digital writing.

1. Introduction

Heterocyclic ligands with metal-coordinating sites along with self-complementary hydrogen bonding sites facilitate supramolecular assembly and directional growth [1,2]. The metal complexes are centre of attention during last several decades for producing network structures with desired properties through self assemblies directed by different metal ions [3–5]. Numerous examples are available in the literature, where heterocyclic ligands having morpholine acts as a coordinating moiety for binding transition metal ions [2,6]. A number of examples are also available in the literature, where heterocyclic molecules along with carboxylate and –OH groups are used for MOFs construction owing to the availability of variable modes of coordination [2,7–9]. Mono and di-carboxylated groups are often useful as they can show a flexible binding mode, and offer interesting multimodal coordination environments for metal ions such as octahedral, tetrahedral or square planar [10]. Heterocyclic molecules are often used for the detection of metal ions owing to their affinity towards metal ions [11] and display an optical response, which may be in the form of a color or change in fluorescence signal [3–5]. In addition, a complex structure formed through the association of metal ion with a heterocyclic ligand may often display porous nature for binding gas molecules or ion binding and can also be used in catalysis [12–15]. The metal–ligand complex in some cases forms a unidirectional assembly, while in other cases they may display a multidirectional growth pattern. Metal complex self-assembled structures are potentially useful in the diverse fields of molecular machines, optoelectronics, semiconductor devices for energy storage etc. [16–18]. Transition metal complexes can also exhibit accessible oxidation and reduction pathways, which helps in accelerating electronic performance [19,20]. Metal complexes with transition metal ion at its central core are also used as molecular magnets [21–23]. The wide applicability of the transition metal complexes in such applications lies in their tendency to flexibly tune intermolecular interactions through ligand modification, which modify their properties to obtain desired results. In this context, small molecule organic linkers are receiving increasing attention in recent times owing to their easy availability, remarkable host–guest response and flexible tendency in achieving supramolecular architecture [24]. In addition, metal–organic complexes can also showcase special geometry and size along with an interesting optical response [25,26]. The development of supramolecular architectures capable of color as well as fluorescence changes upon complexation and solid state fabrication is also of great interest, which can be utilized for on-site and real-time detection of toxic metal ions [27]. Such novel optical detection tools with flexible binding sites, superior signal, and portable features can be of great interest in the area of environmental science [28,29]. Among various utility of transition metal ion complexes, the copper complexes often play a central role in biochemical and enzymatic processes [30,31]. Copper is also an important cation in biochemistry, neurobiology and plays a significant role in enzymatic transformation reactions [32]. The strong ligand binding response of copper and its inherent redox nature imply a

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A light controlled, sensitive, selective and portable spiropyran based receptor for mercury ions in aqueous solution

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Handheld sensors for Hg^{2+} ions
Smartphone based sensors for Hg^{2+} ions
Colorimetric sensor for Hg^{2+} ions
Fluorometric sensors for Hg^{2+} ions
X-ray of spiropyran
Crystal structure

ABSTRACT

A substituted benzothiazolinic spiropyran was synthesized through a reaction between 2-hydroxy-3-methoxy-5-nitrobenzaldehyde and 2-ethyl-3-methylbenzo[d]thiazol-3-ium-4-toluenesulfonate in the presence of piperidine. The spiropyran derivative was characterized using IR, NMR, mass and SCXRD analysis. Owing to the presence of a methoxy group *ortho* to the phenolic oxygen atom, the affinity of the synthesized spiropyran derivative towards toxic metal ions was investigated in CH_3CN: water (1:1). A hypsochromic shift in the absorption and fluorescence spectra was observed in response to the presence of Hg^{2+} ions. The formation of complex was also observed through a visible change in color from dark yellow to colorless. UV–vis, fluorescence spectroscopy and digital image analysis were used to obtain good limit of detection value (5.5 μM, 78.5 nM and 0.62 μM, respectively) for the receptor towards Hg^{2+} ions. The ^1H-NMR spectroscopy indicated the interaction of the phenolic oxygen atom and Hg^{2+} ions. The density functional theory was further used to investigate the stabilities of the different stereoisomers of the spiropyran derivative and their complex. The DFT studies also supported the interaction between the phenolic oxygen atom and the Hg^{2+} ions. TD-DFT studies were also performed to analyze the observed changes in the UV-Visible spectra upon addition of the Hg^{2+} ions, which indicates an increase in the HOMO-LUMO gap.

1. Introduction

A variety of elements are present in our environment, which may be essential or non essential for human life [1–3]. Some metal ions are required for the survival of plants and animals to drive the biological processes, while non-essential elements play no positive role in biological system [1–4]. However, the presence of certain metal ions in excess is toxic to human beings and the environment [5,6]. The toxicity associated with heavy metal ions may be transferred from one organism to others [7,8]. In addition, the non degradative nature of the toxic metal ions may lead to their bioaccumulation [7,8]. The heavy metals such as mercury, cadmium, lead, etc. are considered as highly toxic metal elements in the environment due to their detrimental effects on human health [9,10]. Among these toxic metals, the mercury produce a highly toxic effect on the living organism [9]. Mercury exists in three different oxidation forms: Hg^o, Hg^+ and Hg^{2+} [11,12]. All three forms of mercury are toxic in nature [11]. Absorption of mercury through skin causes different types of skin disease [13]. Minamata disease [14,15] is also caused by mercury poisoning. Mercury poisoning is also responsible for shrinking of our muscles, and serious damage to brain, heart and kidney [16]. Owing to the detrimental effects of mercury, much research is focused on the development of techniques for the detection of Hg^{2+} ion in water and living organisms. Due to the toxicity associated with mercury ions, its presence should be regularly monitored in food materials [17], drinking water [18], and other sources like ponds, rivers and lakes [19]. Techniques like ICP-AES, ion-selective potentiometry, anodic stripping valtammetry and atomic absorption spectrometry are being used for the detection and quantification of metal ions [17,20,21]. The problems associated with instrumental techniques include poor portability, expensive at commercial scale, time consuming, poor selectivity and detection limit. Therefore, there is a need to develop portable and inexpensive materials for the detection of mercury. The optical chemical sensors are worth being explored for the detection of mercury ions owing to their easy availability, simplicity in use and portability to remote areas. In addition, the reuse of sensor may further reduce the cost of the detection process. Optical sensors are available for the detection of different type of analytes in the environmental samples [22–24]. Several types of Hg^{2+} ion sensors are also available, which are usually based on protein [25], gold nanoparticles [16], dimerization of heterocyclic macrocyclic organic

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ORIGINAL ARTICLE

Tweezer-shaped hydrazone derivatives for the selective detection of cyanide ion

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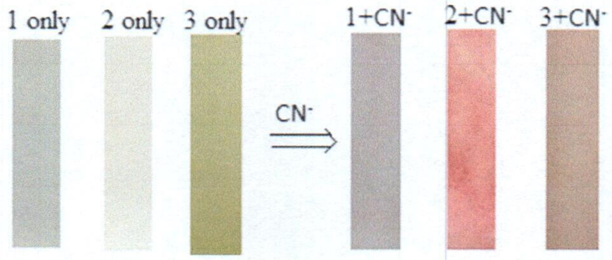
Abstract

A series of hydrazone moiety based probes with variable size of binding cavity flanked by mono-nitro and di-nitro group were synthesized. Characterization of the synthesized probes was performed by using ^{1}H, ^{13}C-NMR, HR-MS and FT-IR spectral techniques. Owing to the presence of N–H moieties and nitro groups in the synthesized structures, the probes were evaluated for the detection of anions. The synthesized receptors selectively detected cyanide ions in acetonitrile solution and displayed a distinct change in color. The change in color and selectivity was observed to be dependent on the cage-size and the number of nitro groups present in the structure of the probe. The DFT studies were also performed to understand the mode of binding and color observed in the probes. The parameters obtained from the DFT data correlated very well with the parameters obtained from experimental data. DFT studies indicated that the abstraction of the second proton is more difficult than the abstraction of the first proton due to the presence of H-bonds.

Graphic Abstract



Keywords Cyanide detection · Optical sensors · Colorimetric detection · DFT analysis · Tweezers shaped receptors

Introduction

The global environmental pollution problems caused by anions released as industrial waste are increasing due to increased industrial activities [1, 2]. The waste released into water bodies is affecting the human population and aquatic life, which are dependent on water bodies for their survival [3]. Finding a clean atmosphere, free of pollutants is an extremely important issue, which has captured global attention. The environmental remediation efforts require monitoring of our water bodies to prevent the harmful effect of pollutants on human health. The monitoring of remote polluted sites can be easily achieved by portable supramolecular host–guest sensing systems, which can display enhanced selectivity and sensitivity. Sensitive and selective colorimetric sensors based on the principle of molecular recognition can be helpful tools in countering such environmental crisis [4]. Therefore, supramolecular

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A Smartphone-Assisted Sensitive, Selective and Reversible Recognition of Copper Ions in an Aqueous Medium

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A photochromic substituted spiropyran (8-methoxy-1,3',3'-trimethylspiro[chromene-2,2'indoline]) was successfully synthesized and its structural integrity was ascertained using spectroscopic methods. Owing to the uniquely positioned methoxy and phenolic groups for potential coordination with a metal ion, it was investigated for the recognition of toxic metal ions. The spiropyran derivative responded to the presence of Cu^{2+} ions in an aqueous solution by displaying a color change visible to the naked eye (colorless to pink). The color change was witnessed due to the Cu^{2+} ion-induced transformation of the closed-form (*spiro*) of the substituted spiropyran derivative into an open merocyanine (MC) form, which complexes the Cu^{2+} ion. The color change was further used for the quantification of Cu^{2+} ion concentration in water using a smartphone captured digital images via pixel intensity analysis. The spiropyran derivative displayed $0.24\pm0.01\ \mu M$, $0.65\pm0.06\ \mu M$ ($0.61\pm0.06\ \mu M$ using paper strips) as the LOD for Cu^{2+} ions using UV-Visible spectroscopy and digital colorimetry, respectively. The density functional theory (DFT) calculations and Job's plot supported the formation of a 2:1 (H: G) complex between the spiropyran derivative and copper ions. The time-dependent DFT (TD-DFT) investigations were also used to understand the color change during the complex formation, which indicated a good correlation between the experimental and theoretical results at the molecular level.

Introduction

Copper is among the most common heavy metal ions that is essential for biological function in small concentration but poses a serious environmental challenge.[1] Copper deficiency in plants can cause inhibition in the growth of branches and loss of sheen of leaves.[2] In humans, copper is commonly found in important organs of the body such as kidney, heart, and liver skeletal muscles.[3] Copper is known to maintain the immune functions,[4] healthy bones[5] and blood vesicles[6] in human body. Deficiency of copper in humans may cause high blood pressure,[7] an increased level of cholesterol[8] and a disease named neutropenia.[9] Exposure to a high concentration of Cu^{2+} ions may also lead to a variety of disorders[10] like Menkes and Wilson's disease,[11] Alzheimer's disease,[12] amyotrophic lateral sclerosis,[13] vomiting, diarrhea, weakness, and stomach pain.[14] Hence, it is critical to monitor the concentration of copper ions in our environment to prevent the accumulation of Cu^{2+} ions in the food and water. A variety of analytical tools are used for the analyses for copper concentration in drinking water[15] and eatable,[16] which include colorimetric[17] (UV-Visible spectroscopy), fluorometric,[18] voltammetric analysis,[19] atomic absorption spectroscopy,[20] inductively coupled plasma mass spectroscopy[21] and chromatographic analyses.[22] In order to enhance the portability, selectivity, and sensitivity of the technique used for the determination of copper ions concentration in water, a variety of materials and scaffolds to bind copper ions were developed.[23] For instance, materials based on quantum dots,[24] nano-particles,[25] nano-rod[26] and synthetic molecular receptors were also developed for copper ion detection in water. The use of colorimetric devices also improves the simplicity and portability of the sensing system. The sensing component is the essential and expensive component of any sensing device. Therefore, if the sensing component molecular unit can be regenerated and reused multiple times, the cost of the metal ion concentration monitoring process may reduce drastically. Chemical or thermal methods of regeneration may lead to decomposition of the sensing material thereby altering its composition. In addition, the chemical method leads to environmental pollution due to the usage of chemicals during regeneration process. Therefore, light responsive systems are advantageous as light can be a convenient tool to regenerate the sensing material. Therefore, the use of light responsive system for coordinating excessive copper ions present in water can provide an effective light reversible system.

Literature reports of a variety of light-responsive systems such as spiropyran or spirooxazines are available for the recognition of copper ions.[23d,27] Photoreversible systems may exist in a highly colored merocyanine (MC) form and a colorless spiro (SP) form, which may interconvert in response to an analyte or light.[23d,27] Such reversible systems may be chemically modified to coordinate metal ions like copper or other toxic ions. The availability of a methoxy group at a unique

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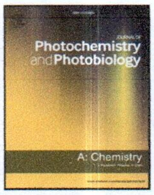

A benzothiazolinic spiropyran for highly selective, sensitive and visible light controlled detection of copper ions in aqueous solution

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ABSTRACT

A benzothiazolinic-spiropyran based optical receptor was synthesized with suitable donor group *ortho* to the phenolic oxygen atom. The structure was established through ^1H, ^{13}C-NMR, HR–MS techniques. Owing to the presence of donor group at a suitable position, it was screened for affinity toward metal ions. The receptor detected the presence of copper ions in aqueous buffered acetonitrile solution by producing a reddish-orange color. The receptor displayed 0.75 μM as the limit of the detection value towards copper ions. The receptor successfully released the copper ions upon irradiation with a light of 532 nm. Test strips coated with spiropyran derivative were developed, which were used for the detection of copper ions in aqueous solution. The DFT calculations indicated that the CTT stereoisomer of the merocyanine form is more stable, while TTT stereoisomer forms the most stable complex with Cu^{2+} ions. The DFT calculations were further used to calculate the pre-organization energies required for the complex formation between the receptor and the copper ions. DFT studies indicated higher than usual stability of the CCC stereoisomer of the merocyanine form, which promoted the reversibility. In addition, the calculations indicated that the copper ion reduced the activation energy barrier for the ring-opening process. TD-DFT calculations were used to investigate the observed absorption band for the receptor and the complex.

1. Introduction

Water pollution caused by increased industrial activities is continuously creating serious environmental issues for the population around the world [1,2]. Among a variety of pollutants released in our water bodies, toxic metal ions present a clear danger to the human population due to their fatal effects on living organisms [1,3]. The toxic metal ions are not degradable that results in their accumulation in the environment and biological system, which further increases the problems associated with them [4,5]. Apart from industries, the sources of toxic metal ions include agricultural, pharmaceutical, geogenic atmospheric sources, mining foundries and domestic effluents [2]. Although the presence of certain metal ions is essential to drive the biological process in a living organism, their presence in excess in food, water or beverages can cause serious ill effects [6–9]. Among different heavy metal ions, the presence of copper ion in trace amount (5–20 micrograms) is essential for carbohydrate metabolism and functions of several enzymes in fish, humans and other mammals [10–12]. The presence of copper ion is also important for haemocyanin and hemoglobin formation [13,14]. However, exposure to the excessive concentration of copper ion can be highly toxic to humans. For example, the copper ion is believed to cause various health effects in humans such as primary biliary cirrhosis, Alzheimer's, Wilson disease, liver, and brain damage [15–18]. Therefore, there is a need to monitor the presence of copper ions in water and other environmental samples. Chemical complexation is usually employed to treat or control the copper ion accumulation in the biological system and the environment [19]. Synthetic chemical receptors are small organic ligands with appropriate functional groups to complex specific analyte [20]. The synthetic chemical receptors on conjugation with a signaling unit can provide an optical signal upon complexation with the analyte (like Cu^{2+} ion) of interest [20,21]. In applications such as sensing of metal ions, the cost of operation can be considerably reduced, if the chemical receptors can be regenerated after use. However, most of the chemical receptor requires harsh conditions for regeneration, which considerably degrade the composition of the receptor samples. The use of visible light to regenerate the receptor may be more desirable as it is convenient and not harmful to humans [20]. Therefore, it is important to develop reversible, photoresponsive systems, which can be used multiple times for the detection of an analyte. In such applications, a photochromic system can be modified using simple chemical reactions to complex metal ions, which may be released in response to light of suitable wavelength [20,22]. In this

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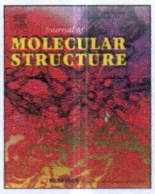

A light controlled, reversible, sensitive and highly selective colorimetric sensor for mercuric ions in water

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ABSTRACT

A merocyanine dye as a *p*-toluenesulfonate salt was synthesized and characterized using spectroscopic techniques. The structure established through single-crystal X-ray crystallography revealed the presence of an extensive H-bond network of dye molecules linked through water molecule and *p*-toluenesulfonate group. The crystal explorer program was used to estimate the contribution of different intermolecular interactions in the network of molecular chains. The addition of mercuric ions led to the disruption of the molecular chains through complex formation between mercuric ions and the merocyanine form, which produced a change in color visible to the naked eye. The molecule displayed no change in color upon addition of other metal ions. The change in color was used for the detection of mercuric ions. The interaction between the dye molecule and the mercuric ion was further investigated using UV–Visible, DLS and ^{1}H NMR spectroscopy. The interaction between the merocyanine dye and the mercuric ions can be reversibly disrupted by UV light (365 nm). The interaction between mercuric ions and the merocyanine dye was further investigated using density functional theory to corroborate the experimental data. TD-DFT studies indicated a increase in the HOMO-LUMO gap upon addition of mercuric ions.

1. Introduction

Rapid industrialization around the world, in search of better living conditions, is creating huge environmental problems as a side effect, which is unsuitable for the health of humans, and can cause disruption of the ecosystem in an extreme case [1,2]. Among a variety of pollutants released as industrial waste into water bodies, mercury ions constitute a serious threat to the health of humans and other living organisms that depend on water bodies for their survival [3–6]. The threat multiplies due to the fact that the metal ions are permeable to the biological membranes and non-biodegradable, which leads to their bio-accumulation. The accumulation of metal ions like mercury affects endocrine and central nervous system [7–9]. Minamata disease and poisoning in Iraq are examples of the effects of excessive mercury on human health [10–12]. The presence of mercury in drinking water may also cause kidney failure, brain damage and other diseases [13–15]. The problem due to mercury poisoning can be further enhanced by methylation of mercury that increases the solubility of mercury in the lipids [16,17].

Therefore, there is a need to develop systems to monitor the concentration of mercuric ion with high sensitivity and reliability in water. Most of the methods available for monitoring the concentration of mercury require sample collection from remote areas followed by their analysis using bulky and expensive instruments, which is time-consuming and costly [18,19]. Therefore, there is a great need to develop a cheaper and portable method for the detection of mercury ions in environmental samples. In this context, synthetic receptors that utilize the principle of molecular recognition are important, which can be used to selectively recognize the mercuric ions at low concentrations with high selectivity through a change in the optical signal [20–22]. A number of receptors that produce both fluorometric and colorimetric signal in the presence of Hg^{2+} ions are available in the literature [23], which are based on small chromophoric groups [7,24–30], quantum dots/nanoparticles/nanoclusters [31–34], DNA/proteins [35–38], synthetic polymers or assemblies [39–43]. Current efforts in this area have focused on to develop receptors that are water-soluble and can be regenerated easily for reuse. In addition, the receptors should display intense signal in the presence of mercuric ion. In this context, photochromic molecules like spiropyran are gaining greater attention due to their easy synthesis,

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