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A pentaquinone-based 4-2 bit photonic encoder[†]

Vandana Bhalla,* Roopa, Ankush Gupta, Abhimanew Dhir and Manoj Kumar*

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A new pentaquinone-based chemosensor armed with phenolic moieties has been synthesized. The fluorescence behaviour of the chemosensor in the presence of different chemical inputs mimics the functions of a digital encoder.

Introduction

Recently, there has been lot of interest in the synthesis of conjugated polycyclic molecules for mimicking the operations of electronic devices in two related but conceptually different fields *i.e.* (a) molecular electronics with current driven functions and (b) molecular switching based on chemical, photonic or electrochemical inputs and outputs.1 Among the different conjugated polycyclic compounds, pentacene is of particular interest because of its high hole mobility in comparison to other organic compounds, and much effort has been devoted to synthesizing pentacenebased derivatives with substituents at different positions.^{2,3} In this regard, a 6, 13 pentaquinone derivative has been used as an important precursor for the design and synthesis of stable and solution-processable pentacene derivatives. However, the role of pentaquinone derivatives in molecular switching with chemical and photonic inputs and outputs, respectively, is still unexplored. Our research work involves the development of chemosensors for the construction of molecular switches and logic-based molecular devices.⁴ In continuation of our research work, we have now designed and synthesized a pentaquinone-based chemosensor that mimics the functions of a 4-2 bit photonic encoder. An encoder is an electronic device, circuit, transducer, software program or algorithm that converts information from one format or code into another for the purpose of standardization, speed, secrecy, security or saving space by size shrinking. There are different types of encoders. A 4-2 bit encoder converts 4 bits of data into 2 bits. Earlier, Andreasson et al.5 reported a molecular encoder based on photochromic systems with different wavelengths as inputs and outputs. Later, Balzani et al. reported a molecular encoder based on bipyridyl system.6 However, a molecular encoder with cations and anions as chemical inputs and fluorescence emission as an output is still unprecedented. The present manuscript focuses on an encoder with ionic chemical inputs. To the best of our knowledge, this is the first report in which a pentaquinone-based derivative has been used for the construction of 4-2 bit photonic encoder.

Experimental

General information

All reagents were purchased from Aldrich and were used without further purification. THF was dried over sodium and benzophenone, and kept over molecular sieves overnight before use. UV-vis spectra were recorded on a SHIMADZU UV-2450 spectrophotometer, with a quartz cuvette (path length, 1 cm). The cell holder was thermostatted at 25 °C. Fluorescence spectra were recorded using a SHIMADZU 5301 PC spectrofluorimeter. ¹H and ¹³C NMR spectra were recorded on a JEOL-FT NMR-AL 300 MHz spectrophotometer using CDCl₃ as the solvent and tetramethylsilane (SiMe₄) as the internal standard. UV-vis studies were performed in dry THF. Data are reported as follows: chemical shifts in ppm (δ), multiplicity (s = singlet, d = doublet, br = broad singlet m = multiplet), coupling constants J (Hz), integration and interpretation. Silica gel 60 (60-120 mesh) was used for column chromatography. Solutions of compound 5 and perchlorate salts were prepared in dry THF.

Synthesis of compounds 1, 2 and 4

Compounds 1, 2 and 4 were synthesized according to procedures reported in the literature.⁷⁻⁹

Synthesis of compound 3

To a solution of **1** (0.8 g, 1.72 mmol) and **2** (0.91 g, 4.14 mmol) in dioxane were added K₂CO₃ (0.95 g, 6.8 mmol), distilled H₂O (8 mL) and [Pd(Cl)₂(PPh₃)₂] (0.302 g, 0.43 mmol) under N₂, and the reaction mixture was refluxed overnight. The dioxane was then removed under vacuum and the residue so obtained treated with water, extracted with dichloromethane and dried over anhydrous Na₂SO₄. The organic layer was evaporated and the compound purified by column chromatography using (95:5 CHCl₃: MeOH) as an eluent to give 0.26 g (31%) of compound **3** as a red solid; mp: >260 °C; ¹H NMR (300 MHz, CDCl₃): δ = 6.63 [d, 4H, *J* = 8.1 Hz, ArH], 7.08 [d, 4H, *J* = 8.4 Hz, ArH], 7.69–7.71 [m, 2H, ArH], 8.07 [s, 2H, ArH], 8.11–8.13 [m, 2H, ArH], 8.93 [s, 2H, ArH], 8.95 [s, 2H, ArH]; MALDI TOF: *m*/*z* 491 (M + 1)⁺. Elemental analysis calc. for C₃₄H₂₂N₂O₂: C, 83.25; H, 4.52; N, 5.71; found: C, 83.10; H, 4.32; N, 5.55%.

Department of Chemistry, UGC-Centre for Advance Studies-1, Guru Nanak Dev University, Amritsar, Punjab, India. E-mail: mksharmaa@yahoo.co.in; Fax: +91 (0)183 2258820; Tel: +91 (0)183 2258802 9 ext. 3205 † Electronic supplementary information (ESI) available. Binding studies of **5** and spectral data. See DOI: 10.1039/c0dt01436b

Synthesis of compound 5

Compound 5 was synthesized by the portion-wise addition of 4 (0.047 g, 0.153 mmol) to a stirred solution of diamine 3 (0.03 g, 0.061 mmol) in (2:1 THF-EtOH). A vellow solid precipitated after refluxing the reaction mixture for 3 d. The solid compound was filtered and washed with ethanol to give 0.03 g of 5 (46%); mp: 160–170 °C; IR v_{max} (KBr pellet, cm⁻¹) 1620 cm⁻¹ (C=N stretching); ¹H NMR (300 MHz, CDCl₃): $\delta = 0.88$ [t, 6H, J =6.45 Hz, CH₃)], 1.27 [br, 36H, CH₂], 1.75–1.82 [m, 4H, CH₂], 3.99 $[t, 4H, J = 6.6 Hz, OCH_2], 6.48 [d, 4H, J = 9 Hz, ArH], 7.21-7.31$ [m, 10H, ArH], 7.70–7.73 [m, 2H, ArH], 8.12–8.15 [m, 2H, ArH], 8.17 [s, 2H, ArH], 8.56 [s, 2H, N=CH], 8.95 [s, 2H, ArH], 8.98 [s, 2H, ArH], 13.71 [br, 2H, OH]; ¹³C NMR (75 MHz, CDCl₃): $\delta = 14.108$ [CH₃], 22.679 [CH₂], 25.976 [CH₂], 29.067 [CH₂], 29.339 [CH2], 29.586 [CH2], 29.627 [CH2], 31.91 [CH2], 68.264 [OCH₂], 101.535 [ArC], 107.708 [ArC], 112.917 [ArC], 120.936 [ArC], 129.483 [ArC], 129.73 [ArC], 130.101 [ArC], 130.859 [ArC], 131.428 [ArC], 133.554 [ArC], 134.428 [ArC], 135.211 [ArC], 138.260 [ArC], 141.969 [ArC], 147.458 [ArC], 161.411 [ArC], 163.751 [ArC], 164.032 [ArC]; MALDI TOF: m/z 1066 (M)+. Elemental analysis calc. for C₇₂H₇₈N₂O₆: C, 81.02; H, 7.37; N, 2.62%; found: C, 81.22; H, 7.29; N, 2.54%.

Results and discussion

The Suzuki-Miyaura cross coupling of compound 17 with boronic ester 2^8 catalyzed by Pd(Cl)₂(PPh₃)₂ furnished diamine 3 in 31% yield (Scheme 1). The ¹H NMR spectrum of **3** showed two doublets (4H each) at 6.63 and 7.08 ppm, two multiplets (2H each) from 7.69-7.71 and 8.11-8.15 ppm, and three singlets (2H each) at 8.07, 8.93 and 8.95 ppm, corresponding to aromatic protons (see ESI Fig. S14[†]). The mass spectrum of compound 3 showed a parent ion peak at m/z 491 (M + 1)⁺ (see ESI Fig. S15[†]). These spectroscopic data corroborate structure 3 for this compound. Further condensation of diamine 3 with 2.5 mol equiv. of 4dodecyloxy-2-hydroxy benzaldehyde 49 furnished compound 5 in 46% yield (Scheme 1). The ¹H NMR spectrum of 5 showed one triplet (6H) at 0.88 ppm for CH₃ protons, a broad signal (36H) at 1.27 ppm for CH₂ protons, a multiplet (4H) from 1.75–1.82 ppm for CH₂ protons, a triplet (4H) for OCH₂ protons, one doublet (4H) at 6.48 ppm, three multiplets (10H, 2H, 2H) from 7.21-7.31, 7.70-7.73 and 8.12-8.15 ppm, three singlets (4H each) at 8.17, 8.95 and 8.98 ppm for aromatic protons, one singlet (2H) at 8.56 for amino protons and one broad signal (2H) for phenolic protons at

13.71 ppm, respectively (see ESI Fig. S16†). The mass spectrum of compound **5** showed a parent ion peak at m/z 1066 (M⁺) (see ESI Fig. S18†). These spectroscopic data corroborate structure **5** for this compound.

The binding behaviour of compound 5 was studied toward different cations and anions by UV-vis and fluorescence spectroscopy. All the titration experiments were carried out in dry THF by adding aliquots of different metal ions. The absorption spectrum of 5 (1 \times 10⁻⁵ M) is characterized by the presence of a typical absorption band at 362 nm (see ESI Fig. S3[†]). Of the various metal ions tested (Cu2+, Hg2+, Pb2+, Zn2+, Ni2+, Cd2+, Fe³⁺, Fe²⁺, Ba²⁺, Co²⁺, Ag⁺ K⁺, Na⁺ and Li⁺), a new band was formed at 391 nm upon the addition of 100 equiv. of Hg²⁺ and Fe³⁺ ions (see ESI Fig. S3 and S4, respectively[†]). It was observed that two isosbestic points at 345 and 377 nm were formed upon the addition of Fe³⁺ ions to the solution of 5 (see ESI Fig. S4[†]). However, only one isosbestic point at 345 nm was observed upon the addition of Hg²⁺ ions (see ESI Fig. S3[†]), indicating that both ions interact with 5 in contrasting modes. The formation of a new band at 391 nm is attributed to an intramolecular charge transfer (ICT) mechanism occurring in the presence of Fe³⁺ and Hg²⁺ ions. In addition to cation binding properties, we also investigated the sensing properties of 5 towards different anions (CN⁻, F⁻, Cl⁻, Br⁻, I⁻, HSO₄⁻, CH₃COO⁻, H₂PO₄⁻ and NO₃⁻) using tetrabutylammonium as the counter-cation. Upon the addition of increasing amounts of F⁻/CN⁻ (0-500 equiv.) ions to solutions of 5, the absorption peak at 362 nm gradually moved to a longer wavelength, finally reaching a maximum value at 420 nm with an isosbestic point at 406 nm (see ESI Fig. S5[†]). We also carried out the UV-vis titration of 5 with a relatively strong base, Bu₄NOH, which is known to deprotonate phenolic moieties. It was observed that upon the addition of Bu₄NOH to a solution of 5, a new band corresponding to the deprotonated form of 5 was formed at 465 nm with an isosbestic point at 435 nm (see ESI Fig. S6[†]). On basis of these results, we propose that the UV-vis spectral changes in Fig. S3 and S4 are due to the formation of a hydrogen bond between the phenolic proton and F⁻/CN⁻.

The fluorescence emission spectrum of 5 $(1 \times 10^{-5} \text{M})$ in THF showed a characteristic emission band at 550 nm when excited at 340 nm (Fig. 1), which is attributed to a very fast enol-imine (5a) to keto-amine (5b) tautomerism, involving the phenomenon of excited state intramolecular proton transfer (ESIPT) (Scheme 2). Upon the addition of Hg²⁺ ions to a solution of 5, significant changes were observed in the emission spectra. Upon the addition of 2 equiv. of Hg²⁺ ions, a slight decrease in the emission band of 5



Scheme 1







Fig. 1 Fluorescence spectra of 5 (1×10^{-5} M) in response to the presence of Hg²⁺ ions (0–340 equiv.) in THF; $\lambda_{ex} = 340$ nm.

at 550 nm was observed (Fig. 1). On addition of 2.5 equiv. of Hg²⁺ ions, the fluorescence emission increased again and reached its original value with the appearance of a new blue-shifted band at 461 nm (Fig. 1). Both the bands at 550 and 461 nm increased simultaneously upon the addition of 340 equiv. of Hg²⁺ ions (Fig. 1). Upon further addition of Hg^{2+} ions (560 equiv.), the band at 461 nm increased continuously, while the band at 550 nm slowly disappeared (see ESI Fig. S7[†]). These results proclaim that the subsequent addition of Hg²⁺ ions to the solution of 5 results in inhibition of ESIPT with the simultaneous formation of a supramolecular complex with inhibition of the photoinduced electron transfer (PET)¹⁰ from the imino nitrogen atoms to the phenolic moiety. The binding constant (log β_1) of 5 with Hg²⁺ ions was found to be 5.23 using the non-linear regression analysis program SPECFIT,¹¹ which gave a good fit for a 1:1 species. Job's plot¹² also proved 1:1 stoichiometry (host/guest) (see ESI Fig. S9[†]). The fluorescence quantum yield $(\phi_f)^{13}$ of compound 5 in its free and Hg²⁺-bound state was found to be 0.06 and 0.28, respectively, which proved its reliability as a good Hg²⁺ sensor. This assumption was confirmed with the help of the IR spectrum of 5, in which the peak at 1620 cm⁻¹ and a broad band at 3441 cm⁻¹, ascribed to C=N and OH stretching, respectively, were found to shift to lower wavenumbers of 1614 and 3432 cm⁻¹, respectively, upon Hg²⁺ binding (see ESI Fig. 19 and 20[†]). Thus, we believe that the coordination of Hg²⁺ ions to 5 occurs through imino nitrogen and phenolic oxygen atoms. The signals in the ¹H NMR spectrum of 5 broadened upon the addition of 1.0 equiv. of Hg^{2+} ions $CDCl_3: CD_3CN$ (8:2), which indicates the formation of a complex between 5 and Hg²⁺ ions. Under the same conditions as used above for the Hg²⁺ ions, we also tested the fluorescence behaviour of receptor 5 toward metal ions such as Cu²⁺, Pb²⁺,

 Zn^{2+} , Ni^{2+} , Cd^{2+} , Fe^{3+} , Fe^{2+} , Ba^{2+} , Co^{2+} , Ag^+ , Na^+ , K^+ and Li^+ . The addition of 1000 equiv. of these metal ions guenched the fluorescence emission of 5 to different extents (see ESI Fig. S12[†]), except for Fe³⁺, which showed the complete quenching of the emission of 5 (see ESI Fig. S11^{\dagger}). Thus, it is obvious that the Fe³⁺ ion coordinates in a different manner to the Hg2+ ion, as revealed by UV and fluorescence studies. We propose that the Fe³⁺ ion probably coordinates only with the phenolic oxygen atom, which causes the inhibition of ESIPT, quenching the emission band at 550 nm. The binding constant (log β_1) of 5 with Fe³⁺ ions was found to be 5.13 using the non-linear regression analysis program SPECFIT,¹¹ which gave a good fit for a 1:1 species. Job's plot¹² also proved a 1:1 stoichiometry (host/guest) (see ESI Fig. S9⁺). We also carried out a reversibility experiment that proved that Fe³⁺ binding to compound **5** is reversible. The addition of 3000 equiv. of tetrabutyl ammonium fluoride (TBAF⁻) to the 5.Fe³⁺ complex restored the fluorescence signal of 5, which is ascribed to the affinity of fluoride ions for Fe³⁺ ions (see ESI Fig. S21[†]). We also investigated the binding behaviour of 5 towards various anions (CN⁻, F⁻, Cl⁻, Br⁻, I⁻, HSO₄⁻, CH₃COO⁻, H₂PO₄⁻ and NO₃⁻) by fluorescence spectroscopy under the same conditions as used for the cations. It was observed that upon the addition of only F- and CN-, the emission at 550 nm was quenched, and on further addition, a new band was formed at 461 nm, which was continually enhanced up to the addition of 3000 equiv. of F^- (see ESI Fig. S8[†]) and CN⁻ ions (Fig. 2). This fluorescence behaviour of 5 towards F⁻ and CN- is ascribed to the formation of hydrogen-bonded species (vide supra). The binding constant (log β_1) of **5** with CN⁻ and F⁻ ions was found to be 4.89 and 4.57, respectively, using the nonlinear regression analysis program SPECFIT,¹¹ which gave a good fit for a 1:1 species. Job's¹² plot also proved a 1:1 stoichiometry



Fig. 2 Fluorescence spectra of 5 (1×10^{-5} M) in response to the presence of CN⁻ ions (0–3000 equiv.) in THF; $\lambda_{ex} = 340$ nm.

Table 1 Truth table						
Sr no	. Input 'D	o' Input 'I	D ₁ ' Input 'l	D ₂ ' Input	'D ₃ ' Output	'X'Output 'Y'
1	1	0	0	0	0	0
2	0	1	0	0	0	1
3	0	0	1	0	1	0
4	0	0	0	1	1	1

for CN^-/F^- ions (host/guest) (see ESI Fig. S10⁺). The addition of other anions, except for F^- and CN^- , quenched the fluorescence emission of **5** to different extents (see ESI Fig. S13⁺).

In the above experiments, high equivalents of cations and anions were added to solutions of compound **5** to generate an appropriate fluorescence response. The use of high equivalents of cations/anions is due to an efficient ESIPT phenomenon that is prevalent in compound **5**. In the case of anions, another reason could be the weak acidity of the phenolic protons.

There has been a lot of interest in the development of materials that could protect information at the molecular level. Molecular keypad locks have been developed for this purpose.^{14,4c,4d} However, the amount of data that can be protected or the quantity of information stored has not been taken into consideration while developing these keypad locks. An encoder is a device that can also compress data for storage and transmission. It converts coded inputs into other coded outputs. Hence, the compressed data is also hidden and protected. Therefore, an encoder can perform both the function of protector and compressor of information. Thus, in continuation of our research program to mimic electronic devices, we examined our system as a molecular encoder. To acquire a 4-2 bit photonic encoder, we envisaged $\mathbf{D}_0 = \mathrm{Fe}^{3+}$ (1000 equiv.), \mathbf{D}_1 = CN^{-} and F^{-} (3000 equiv.), $D_2 = [\{Cu^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, Ni^{2+}, Cd^{2+}, Ni^{2+}, Ni^{2+}, Cd^{2+}, Ni^{2+}, Ni^{2+},$ Fe²⁺, Ba²⁺, Co²⁺, Ag⁺, Na⁺, K⁺ and Li⁺} (1000 equiv.) {Cl⁻, Br⁻, l⁻, $HSO_4^-, CH_3COO^-, H_2PO_4^- and NO_3^-$ (3000 equiv.) and $D_3 = Hg^{2+}$ (340 equiv.) as four chemical inputs and emission wavelengths of 550 and 461 nm as two photonic outputs, 'X' and 'Y', respectively. By the operation of input D_0 to system 5, the emission at 550 nm gets quenched and there is no output emission at 461 nm (see ESI Fig. S11[†]), *i.e.* both outputs 'X' and 'Y' are in the off state '0' (Truth table 1). Reset of the system is achievable upon the addition of F^- ions (vide supra). The operation of input D_1 to the system quenches the emission at 550 nm and forms a band at 461 nm, *i.e.* output X is in the off state '0' and output 'Y' is in the on state '1' (Truth table 1) (see ESI Fig. S8[†] and Fig. 2). The operation of input D_2 to system 5 quenches the emission at 550 nm to a certain extent (see ESI Fig. S12 and 13[†]). Thus, output X is in the on state '1' and output 'Y' is in the off state '0'.

When system 5 is operated by input D_3 , the emission intensity is observed at both wavelengths (Fig. 1). Therefore, both outputs 'X' and 'Y' are in the on state, *i.e.* '1' (Truth table 1).

From truth table 1, the outputs are expressed as:

$$X = D_2 + D_3; Y = D_1 + D_3$$

Therefore, a logic diagram for the 4-2 encoder is obtained, as shown in Fig. 3.

Conclusions

In conclusion we have designed and synthesized a new chemosensor based on a pentaquinone derivative that mimics a 4-2 bit



Fig. 3 Logic circuit of the 4-2 bit encoder.

encoder. Such molecules could replace traditional electronic elements for use in computing and data communication.

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