CHEMISTRY
AN ASIAN JOURNAL
www.chemasianj.org

Accepted Article

Title: Topology-Controlled AIEE of Iminocoumarin Luminophores

Authors: Debasish Haldar, Deepta Chattapadhyay, Sahabaj Mondal, and Santosh Kumar

To be cited as: *Chem. Asian J.* 10.1002/asia.202100590

Link to VoR: https://doi.org/10.1002/asia.202100590

A Journal of
ACES
Asian Chemical Editorial Society

A sister journal of **Angewandte Chemie** and **Chemistry – A European Journal**

WILEY-VCH

Topology-Controlled AIEE of Iminocoumarin Luminophores

Deepta Chattapadhyay,[a]¶ Sahabaj Mondal,[a]¶ Santosh Kumar,[a] and Debasish Haldar*[a]

Dedication ((optional))

[a] Deepta Chattapadhyay , Sahabaj Mondal, Santosh Kumar and Dr. Debasish Haldar
Department of Chemical Sciences and centre for Advance Functional Materials and Centre for Climate and Environmental Studies,
Indian Institute of Science Education and Research Kolkata
Mohanpur 741246, West Bengal, India
E-mail: deba_h76@iiserkol.ac.in; deba_h76@yahoo.com
¶ contributed equally to this work

Supporting information for this article is given via a link at the end of the document.

Abstract: Aggregation-induced emission enhancement (AIEE) is an unusual phenomenon where luminophores show higher photoluminescence efficiency in the aggregated and solid-state. We report the design and synthesis of a series of luminophores **1**-**4** with imine functionality at 6 position of coumarin and studied their AIE propensities on self-assembly. The effect of the topology of the phenolic hydroxyl group on the emission behaviour of the luminophores has been investigated. The imines show significant solvatochromism with high emission in non-polar solvents, whereas the emission gets quenched in the polar solvent. The fluorescence in the toluene-hexane mixture arises due to the aggregation of fluorophores and falls under the category of AIEE. Not only the solution state emission of the isomeric iminocoumarin luminophores is notably varied, but also their solid-state emission found to be significantly different from each other. Moreover, the iminocoumarin **1** selectively recognizes Fe(III) over Fe(II) with a prominent color change. In situ oxidation of Fe(II) with H_2O_2 exhibits the same effect like Fe(III) and developed a chemical combinational logic gate.

Introduction

Fluorescent dyes with efficient emissions in the aggregate have attracted considerable attention over the past two decades.[1-3] Many such materials have found their increasing application in the field of optoelectronics, such as light-emitting diodes[4,5], optical data storage[6], as well as sensing, analytical chemistry,[7-9], and life sciences.[10-13] The optical and electronic properties of such materials in the devices are determined by the constituent molecules' chemical structure and also largely dependent on their aggregation propensities. Many fluorescent organic molecules that show high emission in solution are not efficient emitters in the solid-state. This happens because of increased overlap between π-orbitals of neighboring molecules in closely packed head-to-head arrangements that facilitate delocalization of excitons and increase charge carrier mobility.[14,15] Such phenomena open up certain new pathways for non-radiative decay, leading to a drop of solid-state luminescence, which is commonly referred to as concentration quenching.[16,17] Even though the photophysical properties in dilute solutions had been studied extensively over several decades,[18-22] the emission properties in aggregate state are gaining interest more recently.[23-25] Tang and coworkers have reported the solid-state emission of pentaphenylsilole[26] and tetraphenylethene (TPE),[27] and claimed that aggregation-induced emission depends first and foremost on the control over non-radiative decay and applied the restriction of the intramolecular rotation to control the non-radiative decay.[28] Hence, the structure-property relationships may shed some light on aggregation-induced emission from luminogenic solid.[29–33] It would be also interesting to design new molecules and control their aggregation-induced emission.

In this context, we have designed and synthesized a series of luminophores **1**-**4** with imine functionality at the 6 position of coumarin and investigated their AIE propensities. Coumarin generally emits in the blue-green region and has been used as dye for lasers and sensors.[34-36] Ting and co-workers have exploited the coumarin ligation technique for imaging protein-protein interactions inside a living cell.[37] Recently there have been several reports on solid-state optical properties of coumarin-based fluorophores.[38-41] So far, few coumarin-based compounds have been known to exhibit fluorescence in solid-state. However, iminocoumarins are one of the less explored classes of coumarins for their solid-state luminescence.[42-44] For iminocoumarin luminophores **1**-**4**, we have studied the effect of the topology of the phenolic hydroxyl group on their emission behavior. The luminophores show significant solvatochromism with high fluorescence in non-polar solvents, but the fluorescence quenched in a polar solvent. The emission of the iminocoumarin luminophores in toluene-hexane mixture appear due to aggregation. The solution state fluorescence of the isomeric iminocoumarin luminophores is varied notably. In addition, their solid-state emission also differs significantly. Furthermore, the luminophore **1** recognizes Fe(III) selectively over Fe(II) with a distinct change of color. However, on oxidation of Fe(II) with H_2O_2 shows the same effect like Fe(III) and developed a chemical logic gate.

Results and Discussion

All the luminophores (Figure 1) were synthesized following standard solution phase methodologies, purified, and characterized by ^{1}H NMR, ^{13}C NMR, and Mass spectrometry analysis. All the imine compounds were synthesized using aminocoumarin compound **5** as a precursor.[41] The benzaldehyde, *o*-hydroxy benzaldehyde, *p*-hydroxy benzaldehyde, and *m*-hydroxy benzaldehyde were commercially available. The design principle behind this was to analyze the

10.1002/asia.202100590

effect of additional phenyl rings on the optical properties compared to the precursor coumarin molecule and substituent topology on the optical properties of isomeric luminophores.

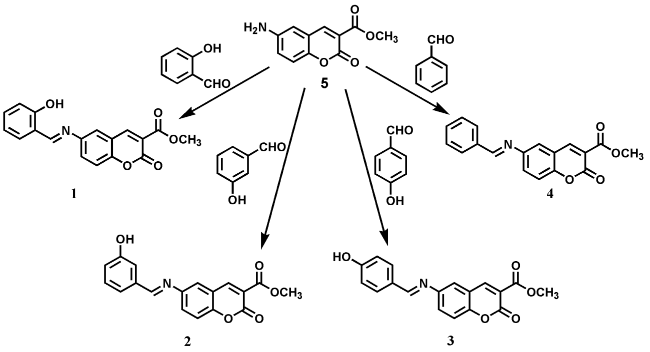


Figure 1. The schematic representation for the synthesis of iminocoumarin luminophores **1**-**4**. Reagents and conditions: 3 drops AcOH, EtOH, reflux, 8h, 80-90% yields.

Firstly, we recorded the UV-Vis absorption spectra of iminocoumarin luminophore **1** in THF solution to see whether there is a difference from reported coumarin peak positions (275 and 335 nm due to $\pi-\pi^*$ transition). It was observed that the compound exhibits two peaks at 288 nm and 347 nm, and the intensity of the band increases with an increase in concentration (Supporting Information Figure S1).

Interestingly, the iminocoumarin **1** shows solvatochromism property with high emission in non-polar solvents and reduced emission intensity in more polar solvents. The emission peak of iminocoumarin luminophore **1** appears at 548 nm in non-polar solvent cyclohexane. (Figure 2a) To further validate the phenomena, we added polar solvent MeOH in cyclohexane solution. We observed a significant decrease in emission intensity when a small amount of MeOH was added. (Figure 2b). Similar phenomena were observed for the iminocoumarin luminophore **2** and **3,** where the –OH group is present in meta and para position, respectively, concerning the imine functionality. Both the compounds were insoluble in hexane or cyclohexane; therefore, we varied the solvents with increasing polarity starting from toluene to acetonitrile. In toluene, iminocoumarin luminophore **2** exhibits an emission peak at 526 nm, whereas the emission spectrum gets significantly red-shifted in slightly more polar solvent ether. (Figure 2c)

The emission gets quenched in solvents with higher polarity. The emission intensity decreases considerably with the addition of 20 μL of THF, which is more prominent when 20 μL of methanol is added instead of THF (Supporting Information Figure S2). In iminocoumarin luminophore **3,** where the hydroxyl group is in the para position, the emission spectra follow the same trend as **1** and **2,** with emission intensity decreasing with an increase in solvent polarity. Emission peak arises at 536 nm in toluene (Figure 2d). Quenching of emission on the addition of polar protic solvent is also observed here (Supporting Information Figure S3). Analyzing these results shows that in non-polar solvents, aggregate formation occurs due to relatively less solubility of the compounds. The emission might be due to those aggregate formations, a phenomenon commonly known as aggregation induced emission enhancement (AIEE).

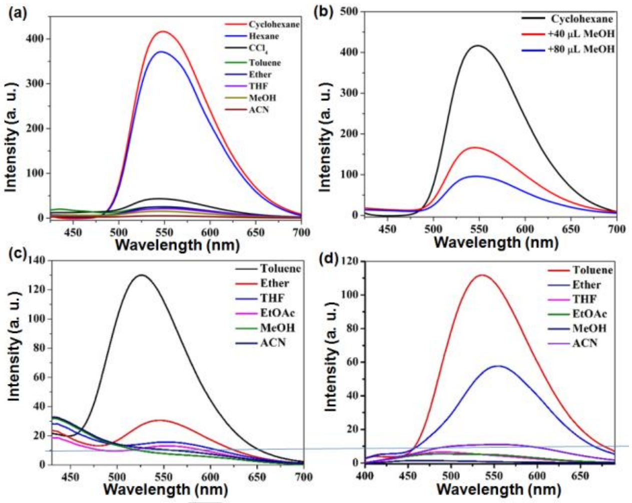


Figure 2. (a) Emission spectra of iminocoumarin luminophore **1** in different solvents, (b) Fluorescence quenching with MeOH addition. [Conc. 10-4 M] (c) Emission spectra of iminocoumarin luminophore **2** in different solvents, (d) Emission spectra of iminocoumarin luminophore **3** in various solvents. [Conc.: 10-4 M].

To probe aggregation-induced emission behavior in solution, the compound of interest is generally first dissolved in an organic solvent like THF or acetonitrile to make a dilute solution and emission spectra is recorded. Then a non-solvent-like water is added to that solution. Since the π-conjugated molecules are most likely to be hydrophobic; under the mixture with high water content, they cluster together to form aggregates, reflected in higher emission in the mixture relative to the pure solution. However, the challenge in our case is that iminocoumarin luminophores are prone to hydrolysis in an aqueous mixture. Therefore, we designed an alternate method to do the experiment. Since iminocoumarin luminophores **2** and **3** are insoluble in hexane, we used hexane as a non-solvent for these molecules. The emission spectra were first recorded in toluene (Conc. 4 X 10^{-5} M). Then emission in different toluene-hexane fractions was measured, keeping the compound concentration fixed. A gradual increase in the emission intensity was recorded for both the compounds with an increase in hexane fraction in the mixture (Figure 3a, c), which indicates AIEE for these compounds.

To probe the aggregation phenomenon of iminocoumarin luminophores **2** and **3**, we have performed DLS studies. In 100% toluene, the luminophore **2** has particles with an average diameter of 14 nm. However, in 80% toluene and 20% hexane, the average diameter of the aggregation increases to 20 nm (Figure 3b). With % increase of hexane, the size of the luminophore **2** aggregation keeps increasing, and at 20% toluene and 80% hexane, the average diameter of the aggregate is 470 nm (Figure 3b). The same phenomenon was observed for iminocoumarin luminophore **3**. In pure toluene, the luminophore **3** exhibits particles having a diameter of ca. 24 nm (Figure 3d). With the increasing % of hexane in toluene, the size of the luminophore **3** aggregates is increasing, and at 20% toluene and 80% hexane, the average diameter of the aggregate is 500 nm (Figure 3d).

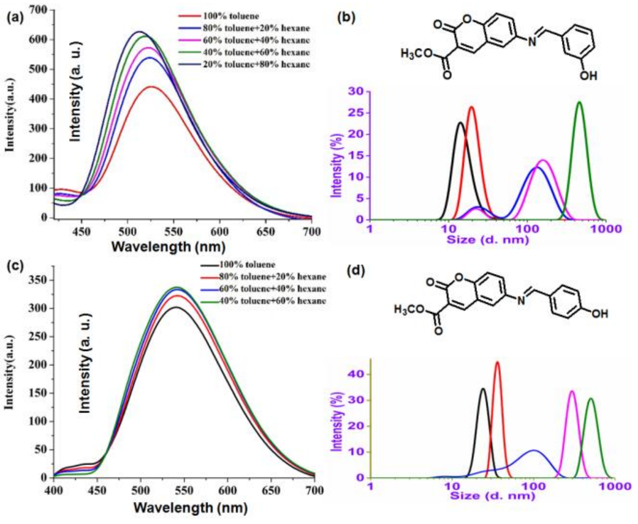


Figure 3. (a) Emission spectra are showing aggregation-induced emission enhancement (AIEE) of iminocoumarin luminophore **2** (b) DLS studies showing the enhancement of the aggregate size of iminocoumarin luminophore **2** with the amount of hexane in toluene**.** (c) Emission spectra show aggregation-induced emission enhancement (AIEE) of iminocoumarin luminophore **3** (d) DLS studies showing the enhancement of the aggregate size of iminocoumarin luminophore **3** with the amount of hexane in toluene**.** (Excitation: 366 nm)

The aggregation phenomenon of iminocoumarin luminophores **2** and **3** was also studied by polar optical microscopy (POM). The sample prepared with iminocoumarin luminophores **2** in 100% toluene exhibits disperse tiny aggregates under POM (Supporting Information Figure S4). However, the sample prepared from iminocoumarin luminophores **2** in 20% toluene and 80% hexane shows significantly bigger aggregates under POM (Supporting Information Figure S4). Similar results were obtained by sample prepared from iminocoumarin luminophores **3** in 100% toluene or 20% toluene and 80% hexane (Supporting Information Figure S5).

We have also studied the solid-state photoluminescence of the iminocoumarin luminophores **1**-**4**. We also measured solid-state luminescence of precursor aminocoumarin **5** for comparison. Photoluminescence for all the compounds was measured for powdered sample in HORIBA Fluoromax spectrofluorimeter. Under 366 nm excitation wavelength (Figure 4a). It was observed that the aminocoumarin **5** gives significantly red-shifted solid-state emission with emission peaks arising at 601 nm (Figure 4a). Although not much difference was observed in the spectral peak position in solution state emission for the iminocoumarin luminophores **1**-**4**, their solid-state emission varied much from one compound to another. In addition, the emission spectra in powder appear to feature more than one emission band (550 nm for compound **3**), with the band at 600-650 nm being the most red-shifted one, though this effect does not show up in solution. It is possible that in the solid state there is a J-aggregation that leads to a new emission band. The iminocoumarin luminophore **1** with a phenolic hydroxyl group at ortho position showed the strongest emission amongst all with 5-fold emission intensity as compound **5**. This is due to the stable six membered intramolecular hydrogen bond (Supporting Information Figure S6). It emits in the yellow region with an emission peak at 574 nm (Figure 4a). The iminocoumarin luminophore **3** with a phenolic hydroxyl group at para position gives the second most intense emission profile in the class, and the emission is slightly red-shifted (Figure 4a). The emission peak appears at 630 nm, although a shoulder peak is observed in the green region. To ascertain the existence of multiple emission bands, we have measured the emission lifetime (Supporting Information Figure S7). The compound **2** has shown a single excited state having a lifetime of 9.95 ns, whereas compound **3** has shown two excited states having lifetime 4.6 and 1.8 ns, respectively. Iminocoumarin luminophore **2,** in which phenolic hydroxyl group is at meta position, also significantly differs from solution state emission. Compared to the solution-state peak at 526 nm, the solid-state emission peak appears at 626 nm, although the intensity is comparatively less (Figure 4a). However, iminocoumarin luminophore **4,** with an absence of the phenolic hydroxyl substituent, shows a blue-shifted emission profile; the emission peak is 557 nm (Figure 4a). Thus the iminocoumarin luminophores show a significant difference in intensity and peak position in their solid-state emission, which is quite different from their solution state behavior.

Figure 4b depicts the emission of the solid powder of iminocoumarin luminophores **1**-**4** and aminocoumarin **5** under 366 nm light. Hence, the colours of the emissions from the aggregates of luminophores can be tuned from green to yellow to brown and finally to orange by simply changing the position of the hydroxyl group on the phenyl rings (Figure 4b). An apparent trend has been observed in these isomeric AIEE that the emission colour is red-shifted with increasing electron-donating power of the substituent on the phenyl ring.

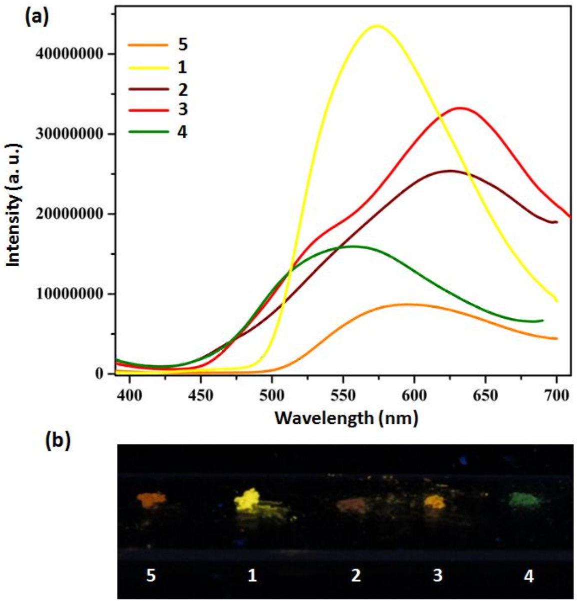
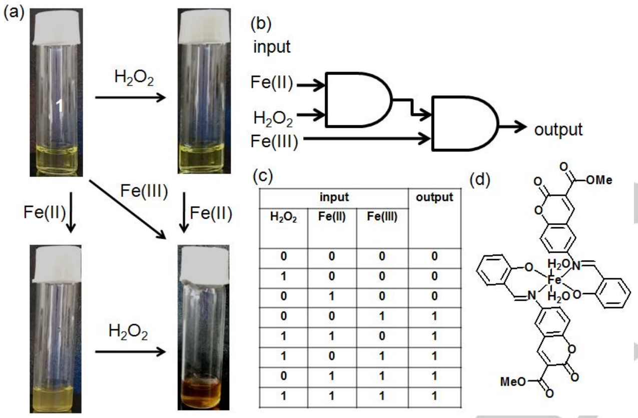


Figure 4. (a) Solid-state emission spectra of the iminocoumarin luminophore **1-4** and aminocoumarin **5**, (b) The powdered samples of iminocoumarin luminophore **1-4** and aminocoumarin **5** under 366 nm U.V. light.

Moreover, iminocoumarin luminophore **1** can selectively recognize Fe(III) over Fe(II), and the colour of the solution changes from yellow to brown (Figure 5a and Supporting Information Figure S8). This is due to the formation of a soluble

Fe(III) complex (Figure 5d). To obtain information on the association constant, we have also done the titration of Fe(III) with compound **1** (Supporting Information Figure S9) and a Job Plot (Supporting Information Figure S10) and Stern Volmer plot (Supporting Information Figure S11). The stoichiometry is 2:1 for compound 1 : Fe(III). The value of the association constant is 0.17 x 10^4 M^{-1}.Utilizing this fact that iminocoumarin **1** can selectively recognize Fe(III) over other ions (Supporting Information Figure S12), we have developed a combinational logic gate system based on three inputs such as Fe(III), Fe(II), and an in situ oxidizing agent H_2O_2, and one output (Figure 5b). In the combinational logic gate, the presence and absence of Fe(II), H_2O_2, and Fe(III) were designated as inputs 1 and 0 (Figure 5c). No change in color was assigned as 0 and 1 if color changed to brown in the output. The input signals other than 000, 010 and 001, show colour change to brown (output 1) and thus mimic the AND logic gate. Furthermore, the AND gate output with Fe(III) develops the OR logic gate. We have also tried other available oxidizing agents such as $NaNO_2$ and *m*-chloroperbenzoic acid. We have obtained same results but the rate ware quite slow.



input			output
H_2O_2	Fe(II)	Fe(III)	
0	0	0	0
1	0	0	0
0	1	0	0
0	0	1	1
1	1	0	1
1	0	1	1
0	1	1	1
1	1	1	1

Figure 5. (a) Fe(III) sensing by the iminocoumarin luminophore **1**. (b) Schematic of the logic gate. (c) Combinational logic gate system based on three inputs, (d) Proposed Fe(III) complex with iminocoumarin luminophore **1**.

Conclusion

In conclusion, this work demonstrates the enhancement of the emission of iminocoumarin luminophores due to the aggregation in solution and solid-state. In particular, we report the effect of the position of the phenolic hydroxyl group on the emission behavior of the isomeric luminophores. The imines show significant solvatochromism with high emission in non-polar solvents, whereas the emission gets quenched in polar solvents. The fluorescence in the toluene-hexane mixture arises due to the aggregation of the fluorophores and falls under the category of AIEE. Not only the solution state fluorescence of the iminocoumarin luminophores is significantly varied, but also their solid-state emission found to be notably different from each other. Moreover, the iminocoumarin **1** selectively recognizes Fe(III) over Fe(II) with yellow to brown colour change. In situ oxidation of Fe(II) with H_2O_2 exhibits the same effect like Fe(III) and developed a chemical combinatorial logic gate. This study opens a new direction of topology-controlled AIEE properties of conjugated organic molecules and the possibility to design new functional materials.

Experimental Section

Synthesis

The aminocoumarin **5** was synthesized following the reported procedure.[41] The compound **5** was taken in a 100 mL flask and dissolved in 30 mL absolute ethanol. Aromatic aldehyde was added, followed by 2-3 drops of acetic acid. The mixture was stirred under reflux for 8h with a $CaCl_2$ guard tube. Then the reaction mixture was cooled to room temperature, and a yellow precipitate was observed. The solid precipitate was filtered and washed with ether, and dried under vacuum to obtain pure iminocoumarins. The reaction intermediates and final luminophores were fully characterized by ^1H NMR (400 MHz and 500 MHz) spectroscopy, ^{13}C NMR (100 MHz and 125 MHz) spectroscopy, and mass spectrometry.

NMR Experiments

All NMR spectroscopy was done on a 400 MHz Jeol or 500 MHz Bruker spectrometer. Compound concentrations were in the 1–10 mM range in $CDCl_3$ or DMSO-d_6 solutions.

Mass Spectrometry

Mass spectrometry was carried out on a Waters Corporation Q-Tof Micro YA263 high-resolution mass spectrometer by electrospray ionization (positive-mode).

Absorption spectroscopy

The absorption spectra of the luminophores were measured on a Perkin Elmer UV/Vis spectrometer (Lambda 35) using a quartz cell with a 1 cm path length.

Fluorescence spectroscopy

All fluorescence spectra were recorded on a Perkin Elmer fluorescence spectrometer (L.S. 55) using a 1 cm path length quartz cell. Slit widths of 2.5 nm / 2.5 nm were used.

Solid-state luminescence

Photoluminescence for all the compounds was measured for powdered samples in HORIBA Fluoromax spectrofluorimeter under 366 nm excitation wavelength.

Dynamic light scattering

Particle sizes were measured by dynamic light scattering (DLS), Malvern Zetasizer Nano ZS (Malvern Instruments Ltd., UK) equipped with a He-Ne laser (wavelength: 633 nm). First, we made 10^{-2} (M) stock solution in toluene. Then we made 10^{-4} (M) solution in the respective mix solvent (toluene/hexane). For DLS size measurement, we took 20 μL of the respective mixture in 1mL solvent with a respective toluene/hexane ratio.

Optical Microscopy

Optical microscopy was performed to examine the aggregation of the compounds from the solution. A drop of compound solution was cast on a clean microscopic glass slide and dried under a vacuum. The images were captured in an Olympus polar optical microscope.

Supporting Information

Supporting information contains a detailed description of the experimental section, including synthesis and characterization.

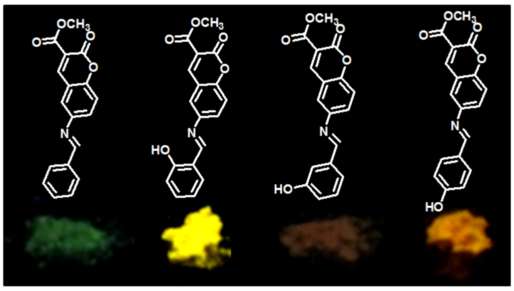
Acknowledgments

This work is supported by IISER-Kolkata, India. D. C. acknowledges DST for Inspire fellowship. S. M. and S. K. are thankful to CSIR, India, for the research fellowship.

Keywords: aggregation-induced emission • iminocoumarin • luminophores • solid-state • logic gate

[1] S. Suzuki, S. Sasaki, A. S. Sairi, R. Iwai, B. Z. Tang, G. Knoishi, *Angew. Chem., Int. Ed.* **2020**, *59*, 9856 – 9867.
[2] X. Wang, O.S. Wolfbeis, R.J. Meier, *Chem. Soc. Rev*. **2013**, *42*, 7834-7869.
[3] S. Varghese, S. Das, *J. Phys. Chem. Lett*. **2011**, *2*, 863-873.
[4] S.R. Forrest, *Nature* **2004**, *428*, 911–918.
[5] Y. S. Zhao, H. Fu, A. Peng, Y. Ma, Q. Liao, J. Yao, *Acc. Chem. Res*. **2010**, *43,* 409-418.
[6] B. H. Cumpston, S. P. Ananthavel, S. Barlow, D. L. Dyer, J. E. Ehrlich, L. L. Erskine, A. A. Heikal, S. M. Kuebler, I.-Y. S. Lee, D. McCord-Maughon, J. Qin, H. Röckel, M. Rumi, X.-L. Wu, S. R. Marder, J. W. Perry, *Nature* **1999**, *398*, 51–54.
[7] R. Petermann, M. Tian, S. Tatsuura, M. Furuki, *Dyes Pigm*. **2003**, *57*, 43-54.
[8] H Li, Cai L, Chen Z. in *Coumarin-derived fluorescent chemosensors; Advances in Chemical Sensors*, (Eds.:W Wang), InTech, **2011**, pp. 121-150. ISBN 978-953-307-792-5.
[9] S. Fery-Forgues, *Nanoscale* **2013**, *5*, 8428-8442.
[10] J. Mei, N. L. C. Leung, R. T. K. Kwok, J. W. Y. Lam, B. Z. Tang, *Chem. Rev.* **2015**, *115*, 11718 – 11940.
[11] J. Mei, Y. Hong, J. W. Y. Lam, A. Qin, Y. Tang, B. Z. Tang, *Adv. Mater.* **2014**, *26*, 5429 – 5479.
[12] Y. Chen, J. W. Y. Lam, R. T. K. Kwok, B. Liu, B. Z. Tang, *Mater. Horiz*. **2019**, *6*, 428 – 433.
[13] Hong Yang, Mengqi Li, Chong Li, Qianfu Luo, Ming-Qiang Zhu, He Tian, Wei-Hong Zhu, *Angew. Chem., Int. Ed.* **2020**, *59*, 8560– 8570.
[14] A. B. Koren, M. D. Curtis, A. H. Francis, J. W. Kampf, *J. Am. Chem. Soc.*, **2003**, *125*, 5040–5050.
[15] M. D. Curtis, J. Cao, J. W. Kampf, *J. Am. Chem. Soc*. **2004**, *126*, 4318–4328.
[16] J. B. Birks, *Photophysics of Aromatic Molecules, Wiley: London*, **1970**.
[17] Y. Hong, J. W. Y. Lama, B. Z. Tang, *Chem. Commun.* **2009**, 4332–4353.
[18] S. W. Thomas III, G. D. Joly, T. M. Swager, *Chem. Rev.* **2007**, *107*, 1339-1386.
[19] F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer, A. P. H. J. Schenning, *Chem. Rev*. **2005**, *105*, 1491-1546.
[20] U. H. F. Bunz, *Chem. Rev.*, **2000**, *100*, 1605-1644.
[21] F. Hide, M. A. Diaz-Garcia, B. J. Schwartz, A. J. Heeger, *Acc. Chem. Res.* **1997**, *30*, 430-436.
[22] S. M. Borisov, O. S. Wolfbeis, *Chem. Rev.* **2008**, *108*, 423-461.
[23] J. Mei, N. L. C. Leung, R. T. K. Kwok, J. W. Y. Lam, B. Z. Tang, *Chem. Rev.* **2015**, *115*, 11718-11940.
[24] J. Mei, Y. Hong, J. W. Y. Lam, A. Qin, Y. Tang, B. Z. Tang, *Adv. Mater.* **2014**, *26*, 5429-5479.
[25] Y. Hong, J. W. Y. Lam, B. Z. Tang, *Chem. Soc. Rev.* **2011**, *40*, 5361-5388.
[26] J. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhuc, B. Z. Tang, *Chem. Commun.* **2001**, 1740 – 1741.
[27] H. Tong, Y. Dong, M. Haubler, J. W. Y. Lam, H. H.-Y. Sung, I. D. Williams, J. Sun and B. Z. Tang, *Chem. Commun.* **2006**, 1133–1135.
[28] J. Chen, C. C. W. Law, J. W. Y. Lam, Y. Dong, S. M. F. Lo, I. D. Williams, D. Zhu, B. Z. Tang, *Chem. Mater.* **2003**, *15*, 1535 – 1546.
[29] J. W. Chen, B. Xu, X. Y. Ouyang, B. Z. Tang, Y. Cao, *J. Phys. Chem. A* **2004**, *108*, 7522-7526.
[30] H. Tong, Y. Hong, Y. Dong, Y. Ren, M. Haeussler, J. W. Y. Lam, K. S. Wong, B. Z. Tang, J. *Phys. Chem. B* **2007**, *111*, 2000.
[31] Q. Zeng, Z. Li, Y. Dong, C. Di, A. Qin, Y. Hong, L. Ji, Z. Zhu, C. K. W. Jim, G. Yu, Q. Li, Z. Li, Y. Liu, J. Qin, B. Z. Tang, *Chem. Commun*. **2007**, 70-72.
[32] Y. Dong, J. W. Y. Lam, A. Qin, J. Liu, Z. Li, B. Z. Tang, J. Sun, H. S. Kwok, *Appl. Phys. Lett.* **2007**, *91*, 011111.
[33] M. Freemantle*, Chem. Eng. News* **2001**, *79*, 29-32.
[34] B.D. Wagner, *Molecules* **2009**, *14*, 210-237.
[35] K. Hara, Z. S. Wang, T. Sato, A. Furube, R. Katoh, H. Sugihara, Y. Danoh, C. Kasada, A. Shinpo, S. Suga, *J. Phys. Chem. B* **2005**, *109*, 15476–15482.
[36] R. J. Nedumpara, K. J. Thomas, V. K. Jayasree, C. P. Girijavallabhan, V. P. N. Nampoori, P. Radhakrishnan, *Appl. Opt.* **2007**, *46*, 1159–1168.
[37] S. A. Slavoff, D. S. Liu, J. D. Cohen, A. Y. Ting*, J. Am. Chem. Soc.* **2011**, *133*, 19769–19776.
[38] Y.F. Sun, S.H. Xu, R.T. Wu, Z.Y. Wang, Z.B. Zheng, J.K. Li, Y.P. Cui, *Dyes and Pigments* **2010**, *87*, 109-118.
[39] S.Y. Park, M. Ebihara, Y. Kubota, K. Funabiki, M. Matsui*, Dyes and Pigments* **2009**, *82*, 258-267.
[40] K. Kubo, T. Matsumoto, K. Ideta, H. Takechi, H. Takahashi, *Heterocycles* **2012**, *84*, 315-321.
[41] A. Pramanik, D. Haldar, *RSC Adv.* **2017**, *7*, 389.
[42] H. Turki, S. Abid, N. Saffon, S. Fery-Forgues, *Dyes and Pigments* **2012**, *94*, 81-87.
[43] N. Abid, H. Turki-Guermazi, K. Khemakhem, S. Abid, N. Saffon, S. Fery-Forgues, *Dyes and Pigments* **2014**, *101*, 164-171.
[44] K. Khemakhem, M. Soulié, R. Brousses, H. Ammar, S. Abid, S. Fery-Forgues, *Chem. Eur. J.* **2015**, *21*, 7927-7937.

Entry for the Table of Contents



Text for Table of Contents. The isomeric iminocoumarin luminophores exhibit significantly different fluorescence in aggregate and solid-state due to aggregation induced emission enhancement. The topology of the phenolic hydroxyl group has dictated the emission behaviour of the isomeric luminophores. The selective detection of Fe(III) over Fe(II) by luminophore **1** helps to develop a chemical combinatorial logic gate.