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Supramolecular control over recognition and efficient detection of picric acid[†]

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Bimetallic Schiff-base Al³⁺ complexes bearing ester functions at the periphery of the ligands are shown to be efficient fluorescent chemosensors for picric acid detection. The prominent role of an association between the chemosensor and the picric acid in the detection process is demonstrated. The detection of picric acid in water is achieved with the sensor deposited on paper.

The detection of explosives has applications in various fields including military affairs, public security, and pollution concerns for humans and ecosystems. Among the molecules referenced as explosives is the class of nitroaromatics such as picric acid (PA), identified as a notorious environmental polluting agent. Besides several highly sensitive and selective analytical methods for the detection of nitroaromatics,¹ fluorescent sensors have been found to be a challenging and interesting alternative owing to their simplicity of operation, their real-time and fast response and their high sensitivity.² Existing classes of fluorescent sensors comprise organic or inorganic conjugated polymers³ and metalorganic architectures.⁴ In parallel, small luminophore molecules appear to be a good option for several reasons: their syntheses are straightforward, and their structures and solubility can be chemically tuned to increase the sensing selectivity. In the past five years, several attractive fluorescent molecular sensors for PA detection have been reported. They have been derived from organic dyes,⁵ aromatic π -conjugated systems⁶ and some have been elaborated from metal complexes.⁷ All of those polymeric and molecular sensors exhibit a turn-off fluorescent response to PA, likely through a host-guest interaction combined with an electron transfer process from the electron-rich fluorophore to

the electron-deficient PA. However, structural evidence of the association complex formed between picric acid and the fluorophore is scarce. A few crystal structures of host–guest adducts have been reported for polycyclic aromatic hydrocarbon based chemosensors^{6e,8} whereas ¹H NMR evidence has been provided for imidazolium and calix[4]arene chemosensors.^{6b,9}

Herein we describe a very efficient PA sensor derived from luminescent Schiff-base aluminum complexes. We show that supramolecular association plays a pivotal role in the sensing capability, and disclose the crystal structure of the host–guest adduct resulting from the aggregation of PA and the sensor molecule. Remarkably, sensing is achieved in solution and in the solid state, the latter allowing the detection of PA in H_2O .

The bimetallic aluminum complexes considered in this study are depicted in Scheme 1. In the following, **1**, **2**, and **3** abbreviate the cationic molecular moieties of $[Al_2L^{Ph}(H_2O)_4(NO_3)_2]\cdot 10H_2O$, $[Al_2L^{IBu}(H_2O)_4(NO_3)_2]\cdot 8H_2O$, and $[Al_2L(H_2O)_4(NO_3)_2]\cdot 2H_2O$, respectively. Derivatives **1** and **2** possess an electron-rich π -conjugated backbone functionalized by ester groups. As a matter of comparison, the complex without the ester moieties, **3**, was also investigated. Their preparation and characterization are provided in the ESI,† as well as the molecular crystal structures for **1** and **3** (Table S1, Fig. S1 and S2, ESI[†]).

The photoluminescence emission spectra of **1**–3 recorded in methanol at 298 K (Table S2, ESI†) were identical in shape and



Scheme 1 Chemical structures of the ester-functionalized complexes 1 and 2, and the parent complex 3 (S stands for solvent molecules).

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Fig. 1 Fluorescence quenching of **1** (1 × 10⁻⁶ M in MeOH/DMSO) upon addition of incremental amounts of PA (1 × 10⁻³ M in MeOH) (λ_{exc} = 450 nm). Pictures show the emission of a solution of **1** in MeOH/DMSO upon addition of solid PA (irradiation under UV lamp at 365 nm).



Fig. 2 ¹H NMR spectra for Job's plot titration of **1** in $CD_3OD/DMSO-d_6$ with PA in CD_3OD . From bottom to top, the mole fraction $r = [\mathbf{1}]/([\mathbf{1}] + [PA])$ are 1; 0.9; 0.8; 0.7; 0.6; 0.5; 0.4; 0.3, 0.1 and 0 (the red dotted line highlights the PA peak displacement).

exhibited a double emission band with maxima at 504 and 529 nm for 1 (Fig. 1) and 2 (Fig. S4, ESI[†]), and were slightly blue shifted compared with those of 3 (518 and 536 nm, Fig. S4, ESI[†]). This shift is induced by the electron withdrawing group at position 5 of the salicylidene ring.¹⁰ The luminescence quantum yields found for 1 ($\Phi = 0.67$) and 2 ($\Phi = 0.56$) are among the highest known for this class of materials.^{7b,10,11} They are also significantly higher than that found for 3 ($\Phi = 0.20$), as anticipated for the ester-functionalized ligands. The higher efficiency obtained for 1 is ascribed to the aromaticity in the ester group, which has been shown to improve the efficiency of the molecule to re-emit the absorbed photons.^{10,11a}

Upon addition of incremental amounts of picric acid, substantial quenching of the emission of 1 and 2 is observed (Fig. 1 for 1, Fig. S4, ESI[†] for 2) whereas there is almost no change in the emission of 3 in the same conditions (decrease of max. 7%, see Fig. S4, ESI[†]). The influence of the R group of the ester (i.e. Ph versus tBu) on the quenching efficiency and sensitivity was evaluated by calculating the Stern-Volmer quenching constant (K_{sv}) from the fluorescence quenching titration. 1 is more efficient in detecting PA with up to 80% of emission quenching versus 70% for 2 (Fig. S5, ESI[†]); K_{sv} = 3586 M⁻¹ for 1 and $K_{sv} = 1815 \text{ M}^{-1}$ for 2 (Fig. S6, ESI[†]). Limits of detection (LOD) and limits of quantification (LOQ) were also evaluated: LOD were 55 μ M (12.6 μ g mL⁻¹) and 168 μ M (38.6 μ g mL⁻¹), and LOQ were 0.17 mM and 0.51 mM respectively for 1 and 2 (Fig. S7, ESI[†]). The above values are remarkable compared to those of other salophen complexes^{7b} and dyes already reported,^{5b} and are comparable with those of most efficient molecular fluorophores.4i,6c A tentative rationalization for the difference between 1 and 2 might be found in the phenyl substituent of the ester functions for 1 that could contribute by additional aromatic interactions with PA.

¹H NMR titration experiments were carried out to highlight possible interactions between PA and the chemosensors. Salient variations during titration of **1** in CD₃OD/DMSO- d_6 with PA in CD₃OD were as follows: the signals of the imine (H1) and tetraphenylene (H2) protons were slightly downfield shifted whereas the two protons H3 and H4 of the salicylidene ring were much more sensitive and were upfield shifted (Fig. 2). Noteworthy, for PA the signal of the proton at δ = 8.98 ppm in a pure sample is found at δ = 8.65 ppm in the presence of **1** (Fig. 2). It remains unchanged for a mole fraction of 1 between 0.9 and 0.5 before being downfield shifted through the molar ratio of 0. These observations suggested that an interaction occurred in the solution between chemosensor 1 and PA. A stoichiometry of 1: PA = 1:1 for the predominant species in the solution was determined by an examination of the chemical shift variations of protons H2 and H3 by the continuous variation method (Fig. S12, ESI⁺). The binding constant of chemosensor 1 towards PA was estimated through independent ¹H NMR titration from the variation of the chemical shift of H3: $K_{\rm a}$ = 728 M⁻¹ was obtained (Fig. S13, ESI[†]). The same experiments were run for chemosensor 2. A smaller association constant value of 273 M⁻¹ was measured assuming a 1:1 stoichiometry between 2 and PA, as for 1 and PA (Fig. S14, ESI[†]). These values are comparable with those obtained by fluorescence measurements with the Benesi-Hildebrand method (Fig. S8 and S9, ESI[†]): 826 and 576 M⁻¹ respectively for 1 and 2. For 3, no shift of proton signals was observed in the presence of PA (Fig. S15, ESI[†]). These results clearly highlight the essential role played by the ester groups at the periphery of the ligand in the adduct formation. NMR experiments show that the signals of both the PA and the aromatic tetraphenylene and salicylidene rings of the chemosensors are quite affected, suggesting close proximity for the two moieties. It is very likely that this supramolecular complex is at the origin of the fluorescence quenching for 1 and 2 in the presence of PA. As seen for 3, in the absence of such a recognition process the quenching of the emission is poor.

During the emission and NMR titration experiments, high concentrations of PA into solutions of **1** afforded the appearance of an orange solid. Single crystals have been obtained by slow inter-diffusion of MeOH solutions of **1** and PA in large excess



Fig. 3 Crystal structure of the host–guest adduct **1.PA** showing the H-bond interactions between PA and the sensor (in dashed lines). H atoms of coordinated MeOH have been omitted for clarity.

(ESI[†]). The crystal structure (Fig. 3 and Fig. S3, ESI[†]) revealed a 1:2 host–guest adduct, **1.PA**, in which two picrate molecules are trapped within the pockets formed by two facing phenyl-ester-functionalized salicylidene moieties of **1**. Hydrogen bonding between the host and the guests is established between the O atoms of the phenolates and the H atoms of the tetraiminophenyl ring with distances of 2.375(3) and 2.396(3) Å for O26···H101 and O19···H131, respectively. It can be noticed that the phenyl ester rings lay almost parallel to the picrate planes suggesting also weak π – π and π –H interactions between these moieties. Such weak supramolecular interactions are likely to favor and stabilize the adduct **1.PA**.

A ¹H NMR spectrum of **1.PA** crystals (in DMSO-*d*₆ for solubility reasons) again reveals a slight shift of the signals of the three protons, H1, H2 and H3, with respect to **1** (Fig. 4), thus confirming that a degree of interaction is still in place between the two ionic parts of the **1.PA** salt even in DMSO. In addition, the orange solid previously obtained during the NMR titration experiments for high concentrations of PA was isolated; its ¹H NMR spectrum perfectly matches that of **1.PA** (Fig. 4). The emissive characteristic of a solution of **1.PA** was also investigated and revealed weak fluorescence (Fig. S11, ESI[†]). This observation confirms that the vanishing of the fluorescence for the ester-functionalized luminophore is related to the establishment of an association between **1** and PA.

DFT calculations were undertaken to estimate the relative positions of the molecular frontier orbitals of **1–3** and PA, as well as for a series of chemically related molecules: 4-nitrophenol, phenol, 4-nitrobenzene, benzene and toluene (Fig. S16 and Table S3, ESI[†]). In the fluorescence quenching process,



Fig. 4 ¹H NMR spectra in DMSO- d_6 for (a) **1**; (b) **1.PA**; (c) the orange solid obtained after addition of excess PA. (The red arrows show the PA signal. The blue dotted lines highlight the peaks that are shifted by the presence of PA).



Fig. 5 Photographs (under 365 nm UV light) of the fluorescence response of **1** on test strips. (a) Blank paper showing blue emission under UV light, (b) paper impregnated with **1** (real colour is greenish yellow) and (c) colour spots created by depositing (A) 5 μ L of H₂O, (B) 5 μ L of 1 × 10⁻⁵ M PA in H₂O, (C) 5 μ L of 1 × 10⁻³ M PA in H₂O, (D) 5 μ L of 1 × 10⁻¹ M PA in H₂O.

those energy levels reflect the ease of transferring an electron from the sensor in its excited state to the analyte in its fundamental state (LUMO). Luminophores 1, 2 and 3 have their LUMO higher in energy than that of PA but lower than those of the other aromatic compounds considered here. Consequently, only PA is anticipated to lead to a charge-transfer process and a subsequent fluorescence quenching. This was indeed confirmed experimentally (Fig. S10, ESI[†]); except for PA, none of the considered molecules altered the luminescence of the sensors, thus confirming their good selectivity in their response to PA. However, while experimental results with PA for 1 and 2 support the anticipated behaviour, there is a deep discordance for 3, for which luminescence is hardly modified. Obviously, favourable positioning of the frontier orbitals is not the unique driving force of charge transfer and the subsequent luminescence quenching. This confirms the importance of the adduct formation in the sensing process.

Finally, we show in Fig. 5 a visual demonstration of the use of solid 1 as a sensor for PA. Whatman[®] filter paper has been impregnated with a solution of $1 (5 \times 10^{-4} \text{ M} \text{ in MeOH/DMSO})$. After drying, the paper was exposed to spots of the aqueous PA solution at various concentrations. The visual detection response was observed under 365 nm UV light and showed the fluorescence quenching with PA concentrations down to 10 ppm. This test also demonstrates that the supported sensor 1 is able to efficiently detect picric acid in water.

In summary, we have identified a novel, highly fluorescent molecule capable of detecting picric acid efficiently, even in aqueous solutions. More importantly, the gathered results show that molecular association and recognition have a pivotal effect on the sensing efficiency. Our observations suggested that the molecular associations detected either in solution or in solid state are conditioned by the presence of ester groups at the periphery of the Schiff base. These associations contribute to the emission quenching of the reported fluorophores by a charge transfer process. It is the combination of the two phenomena, supramolecular association and charge transfer, that is at the origin of the remarkably efficient detection of PA.

Notes and references

- 1 J. S. Caygill, F. Davis and S. P. J. Higson, Talanta, 2012, 88, 14-29.
- 2 M. S. Meaney and V. L. McGuffin, Anal. Bioanal. Chem., 2008, 391, 2557-2576.
- 3 A. Narayanan, O. P. Varnavski, T. M. Swager and T. Goodson III, J. Phys. Chem. C, 2008, 112, 881–884.

- 4 (a) S.-R. Zhang, D.-Y. Du, J.-S. Qin, S.-J. Bao, S.-L. Li, W.-W. He, Y. Q. Lan, P. Shen and Z.-M. Su, *Chem. Eur. J.*, 2014, **20**, 3589–3594;
 (b) B. Gole, A. K. Bar and P. S. Mukherjee, *Chem. Eur. J.*, 2014, **20**, 2276–2291; (c) Y.-S. Xue, Y. He, L. Zhou, F.-J. Chen, Y. Xu, H.-B. Du, X.-Z. You and B. Chen, *J. Mater. Chem. A*, 2013, **1**, 4525–4530;
 (d) S. S. Nagarkar, B. Joarder, A. K. Chaudhari, S. Mukherjee and S. K. Ghosh, *Angew. Chem., Int. Ed.*, 2013, **52**, 2881–2885;
 (e) S. Pramanik, Z. Hu, X. Zhang, C. Zheng, S. Kelly and J. Li, *Chem. Eur. J.*, 2013, **19**, 15964–15971; (f) L. Sun, H. Xing, J. Xu, Z. Liang, J. Yu and R. Xu, *Dalton Trans.*, 2013, **42**, 5508–5513; (g) Y. Yuan, H. Ren, F. Sun, X. Jing, K. Cai, X. Zhao, Y. Wang, Y. Wei and G. Zhu, *J. Mater. Chem.*, 2012, **22**, 24558–24562; (h) S. Barman, J. A. Garg, O. Blacque, K. Venkatesan and H. Berke, *Chem. Commun.*, 2012, **48**, 11127–11129;
 (i) B. Gole, S. Shanmugaraju, A. K. Bar and P. S. Mukherjee, *Chem. Commun.*, 2011, **47**, 10046–10048.
- 5 (a) Y. Xu, B. Li, W. Li, J. Zhao, S. Sun and Y. Pang, *Chem. Commun.*, 2013, **49**, 4764–4766; (b) M. S. Meaney and V. L. McGuffin, *Anal. Chim. Acta*, 2008, **610**, 57–67.
- 6 (a) V. Bhalla, A. Gupta, M. Kumar, D. S. S. Rao and S. K. Prasad, ACS Appl. Mater. Interfaces, 2013, 5, 672–679; (b) B. Roy, A. K. Bar, B. Gole

and P. S. Mukherjee, *J. Org. Chem.*, 2013, **78**, 1306–1310; (*c*) V. Bhalla, A. Gupta and M. Kumar, *Org. Lett.*, 2012, **14**, 3112–3115; (*d*) N. Venkatramaiah, S. Kumar and S. Patil, *Chem. Commun.*, 2012, **48**, 5007–5009; (*e*) Y. Peng, A.-J. Zhang, M. Dong and Y.-W. Wang, *Chem. Commun.*, 2011, **47**, 4505–4507.

- 7 (a) M. Kumar, S. I. Reja and V. Bhalla, Org. Lett., 2012, 14, 6084–6087; (b) M. E. Germain, T. R. Vargo, B. A. McClure, J. J. Rack, P. G. van Patten, M. Odoi and M. J. Knapp, Inorg. Chem., 2008, 47, 6203–6211; (c) M. E. Germain and M. J. Knapp, J. Am. Chem. Soc., 2008, 130, 5422–5423.
- 8 (a) M. Dong, Y.-W. Wang, A.-J. Zhang and Y. Peng, *Chem. Asian J.*, 2013, 8, 1321–1330; (b) A. Pramanik, M. Bhuyan and G. Das, *J. Photochem. Photobiol.*, A, 2008, 197, 149–155.
- 9 F. Zhang, L. Luo, Y. Sun, F. Miao, J. Bi, S. Tan, D. Tian and H. Li, *Tetrahedron*, 2013, **69**, 9886–9889.
- 10 V. Béreau, V. Jubéra, P. Arnaud, A. Kaiba, P. Guionneau and J.-P. Sutter, *Dalton Trans.*, 2010, **39**, 2070–2077.
- 11 (a) V. Béreau, C. Duhayon, A. Sournia-Saquet and J.-P. Sutter, *Inorg. Chem.*, 2012, **51**, 1309–1318; (b) K.-L. Kuo, C.-C. Huang and Y.-C. Lin, *Dalton Trans.*, 2008, 3889–3898.