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Exciplex fluorescence of {[Zn(bipy)$_{1.5}$(NO$_3$)$_2$}]·CH$_3$OH·0.5pyrene}$_n$: a coordination polymer containing intercalated pyrene molecules (bipy = 4,4′-bipyridine)

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We report the first use of fluorescence spectroscopy to probe the environment of the cavities that are present in open framework coordination polymers.

Coordination polymer networks represent a result of applying supramolecular concepts to the design of new functional solids and are well exemplified by compounds in which transition metal centers (nodes) are connected by linear bidentate organic ligands (spacer groups) such as 4,4′-bipyridine (bipy).[1] These supramolecular structures are of interest as they provide opportunity for generating open framework compounds with controllable cavity sizes and they therefore have the potential to exhibit porosity and/or encapsulate organic guest molecules.[1]

We have become interested in the possibility of using fluorescence spectroscopy to study the properties of coordination polymers, in particular the polarity of the cavities within such 2D networks, by using a guest molecule as a polarity-sensitive fluorescent probe. The compound {[Ni(4,4′-bipyridine)$_2$(NO$_3$)$_2$]·2pyrene}$_n$[2], **1**, represents a rare example of a coordination polymer network with an intrinsic polarity-sensitive fluorophore as part of the crystal structure. Furthermore, it is a prototypal example of a compound containing two very different interpenetrating 2D networks:[2,3] a square grid coordination polymer of Ni^{2+} with bipyridine spacer groups, and a noncovalent grid of pyrene molecules. The presence of pyrene, a highly polarity-sensitive fluorescent probe, suggests the potential for using the measured pyrene fluorescence from this compound to study the microenvironment within this 2D coordination polymer network.

Pyrene monomer fluorescence exhibits well-resolved vibronic bands; the relative intensity of the third to first vibronic bands (I_{III}/I_I) has been shown to be correlated to the polarity of the pyrene medium.[4] Furthermore, at high concentration or in certain organized environments, pyrene molecules interact, exhibiting a broad, red-shifted excimer fluorescence. However, we observed negligible fluorescence using front-face emission studies on the solid powder of **1**, presumably because of the well-known ability of transition metal cations to quench pyrene fluorescence.[5] In order to quantify this for the case of Ni^{2+}, we undertook quenching studies of pyrene monomer fluorescence in aqueous solution by Ni(NO$_3$)$_2$. These experiments indicated that the Ni^{2+} cation is indeed an extremely efficient quencher of pyrene monomer fluorescence. Using steady-state Stern-Volmer analysis,[6] and the measured unquenched pyrene monomer fluorescence lifetime of 241 ns, a very large second-order quenching constant k_q of 2.3×10^9 M^{-1} s^{-1} was determined. Thus, the Ni^{2+} in this coordination polymer significantly quenches the fluorescence of the encapsulated pyrene. We subsequently screened other transition metal cations in solution and found that Zn^{2+} exhibited negligible quenching of pyrene fluorescence.

In this contribution we report the synthesis, structure and fluorescence properties of a new coordination polymer containing T-shaped Zn^{+2} nodes, 4,4-bipyridine and pyrene, {[Zn(bipy)$_{1.5}$(NO$_3$)$_2$]·0.5pyrene·MeOH}$_n$, **2**. This can be prepared by layering a methanolic solution of Ni(NO3)$_2$ with a solution of pyrene and 4,4′-bipyridine and forms sharp, well-defined yellow crystals. These crystals exhibit strong fluorescence that can be easily observed by eye upon excitation with a hand-held UV lamp. Fig. 1a presents the full measured fluorescence spectrum from 350 to 700 nm of **2**.† A strong fluorescence band can be seen in the pyrene excimer region, with $\lambda_{F,max}$ = 540 nm, while a relatively weak monomer band is also observed. This indicates that the pyrene molecules are either interacting with each other resulting in excimer fluorescence, or with the bipy molecules in the structure resulting in exciplex fluorescence. Fig. 1b shows just the pyrene monomer region, and indicates that even though the monomer emission is relatively weak, it is still well defined, allowing for determination of the polarity of the pyrene microenvironment, based on the relative intensity of the resolved vibronic bands. For this compound, a value of I_{III}/I_I = 0.76 was obtained, similar to the value of I_{III}/I_I = 0.75 reported for pyrene in methanol[4] and indicating that the pyrene molecules are experiencing a local environment with a polarity similar to that of a methanol solution.

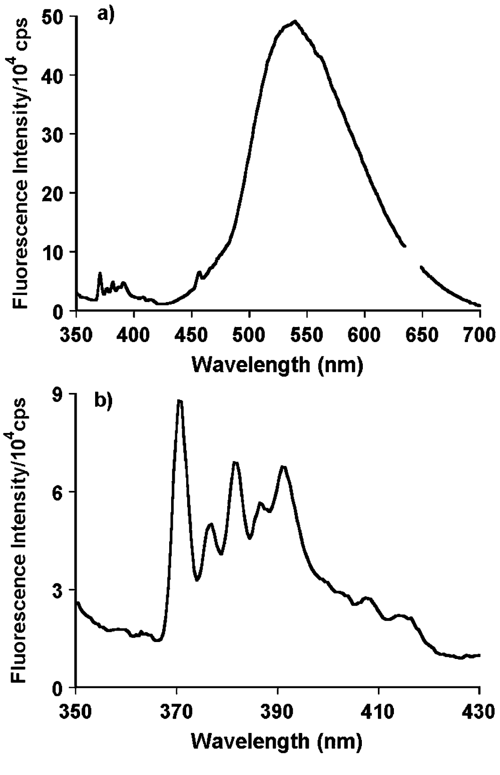

Fig. 1 (a) Fluorescence spectrum of **2** with 320 nm excitation. The gap in data from 635 to 645 nm is due to the large amount of scattered excitation centered at 640 nm, and (b) an expanded view of the pyrene monomer fluorescence region.

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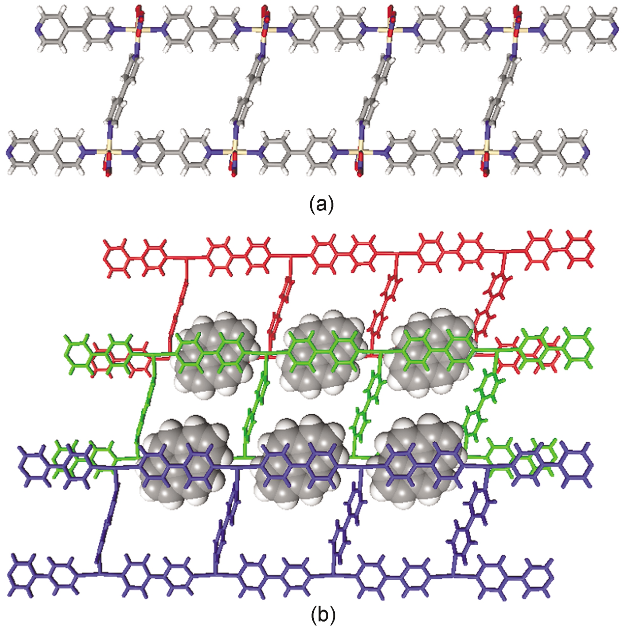
The crystal structure‡ of **2** reveals that the coordination polymer is an open framework molecular ladder[7] based on T-shaped nodes (Fig. 2a) and that the pyrene molecules lie in an environment that is fully consistent with the fluorescence spectrum: sandwiched between 4,4′-bipyridine molecules on ladder networks. This represents an ideal geometry for the formation of a 2 : 1 bipy : pyrene exciplex through π–π interactions (the pyrene–bipy distance is *ca.* 3.7 Å). A wide variety of fluorescent pyrene exciplexes have been reported in the literature, such as those with dimethylaniline ($\lambda_{\mathrm{F,max}}$ = 496 nm in dioxane)[8a] and 4,4′-bis(dimethylamino)diphenylmethane ($\lambda_{\mathrm{F,max}}$ = 460 and 590 nm in cyclohexane).[8b] The latter is especially relevant to the current results, not only because the molecule forming the exciplex with pyrene has two joined phenyl rings (similar to bipy, but joined by a methylene group instead of directly), but also because a 2 : 1 triplex was observed, with a fluorescence band well red-shifted relative to the 1 : 1 exciplex band (590 *vs.* 460 nm). The photophysics of a number of compounds containing both pyrene and bipy have also been reported. In some cases, transition-metal complexes containing bipy and pyrenyl ligands have been prepared;[9] these have shown pyrene monomer and MLCT emission bands. In other cases, pyrene and bipy have been directly covalently coupled; the resulting compounds showed red-shifted emission bands, due to charge transfer from pyrene to bipy through the linking bonds.[10] However, none of these is analogous to the face-to-face arrangement of pyrene and bipy observed in our compound; to the best of our knowledge there has been no previous report of the fluorescence of such an exciplex of pyrene with bipy. We were able to observe a bipy:pyrene exciplex in solution by adding a large amount of bipy to an aqueous pyrene solution (concentration low enough to show monomer fluorescence only); a red-shifted exciplex band was found to grow in intensity as a function of added bipy, with a concomitant loss of monomer intensity. Fig. 3 shows the fluorescence spectrum of such a pyrene/bipy solution, with the red-shifted exciplex band with $\lambda_{\mathrm{F,max}}$ = 435 nm. This band is at a significantly shorter wavelength than that observed from the Zn/bipy/pyrene solid, however in solution the exciplex is presumably 1 : 1, whereas in the solid it is definitely 2 : 1 bipy:pyrene complex. As reported previously, a 2 : 1 exciplex is expected to exhibit red-shifted fluorescence relative to the corresponding 1 : 1 exciplex.[8b]


(a)

(b)

Fig. 2 (a) The open framework ladder coordination polymer in **2** and (b) an illustration of how the pyrene guest molecules in **2** are sandwiched between bipy spacers in adjacent ladders. The distances between the centroids of the bipy pyridyl moieties and the mean plane of the pyrene molecules are between 3.60 and 3.75 Å.

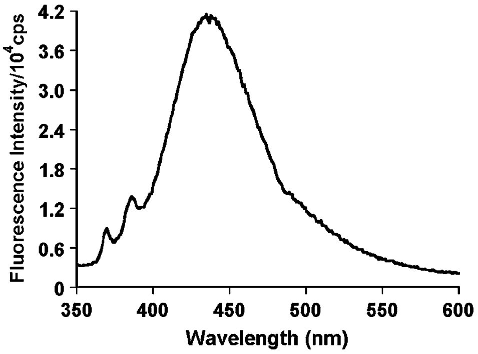


Fig. 3 (a) Fluorescence spectrum of the pyrene–bipy exciplex in water with 340 nm excitation.

In conclusion, a coordination polymer that traps a fluorescent guest has been prepared and characterized for the first time. Strong fluorescence is observable from this solid, and assigned as a 2 : 1 bipy:pyrene exciplex fluorescence. A weak pyrene monomer band is also observable, allowing for estimation that the polarity within this coordination polymer is similar to that of methanol solution.

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Notes and references

† Fluorescence spectra of the solid samples were obtained by direct front-face emission from the solid powder adhered to an aluminium support oriented at 45° to both the excitation and emission light paths, with 320 nm excitation.

‡ Single-crystal X-ray diffraction data of **2** were collected at 173 K on a Bruker-AXS SMART APEX/CCD diffractometer using $\mathrm{Mo}_{\mathrm{K}\alpha}$ radiation (λ = 0.7107 Å): triclinic, $P\bar{1}$, a = 10.0919(7), b = 11.3865(8), c = 12.1526(8) Å, α = 88.1820(10)°, β = 68.5700(10)°, γ = 69.2390(10)°, volume = 1207.82(14) Å^3, Z = 2, ρ_{cal} = 1.528 g cm^{-3}, μ = 1.072 mm^{-1}, $F(000)$ = 570, $2\theta_{\mathrm{max}}$ = 28.27°. Final residuals (for 502 parameters) were $R1$ = 0.0434 and $wR2$ = 0.0985 for 4519 reflections with $I > 2\sigma I$, and $R1$ = 0.0572, $wR2$ = 0.1049 for all 5522 data. Residual electron density was 0.805 and −0.307 e Å^{-3}. CCDC 187761. See http://www.rsc.org/suppdata/cc/b2/b205906a/ for crystallographic files in .cif or other electronic format.

1 M. J. Zaworotko, *Chem. Commun.*, 2001, 1; B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629.
2 K. Biradha, K. V. Domasevitch, B. Moulton, C. Seward and M. J. Zaworotko, *Chem. Commun.*, 1998, 1327.
3 M. Fujita, Y. J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151.
4 K. Kalyanasundaram and J. K. Thomas, *J. Am. Chem. Soc.*, 1977, **99**, 2039.
5 F. Grieser and R. Tausch-Treml, *J. Am. Chem. Soc.*, 1980, **102**, 7258; Y. Nosaka, A. Kira and M. Imamura, *J. Phys. Chem.*, 1981, **85**, 1353; J. C. Dederen, M. Van der Auweraer and F. C. De Schryver, *J. Phys. Chem.*, 1981, **85**, 1198; B. Bodenant, F. Fages and M.-H. Delville, *J. Am. Chem. Soc.*, 1998, **120**, 7511; B. Bodenant, T. Weil, M. Businelli-Pourcel, F. Fages, B. Barbe, I. Pianet and M. Laguerre, *J. Org. Chem.*, 1999, **64**, 7034.
6 L. K. Fraiji, D. M. Hayes and T. C. Werner, *J. Chem. Ed.*, 1992, **69**, 424.
7 P. Losier and M. J. Zaworotko, *Angew Chem., Int. Ed. Engl.*, 1996, **35**, 2779.
8 (*a*) R. J. Hartley and L. R. Faulkner, *J. Am. Chem. Soc.*, 1985, **107**, 3436; (*b*) K. Sen, S. Banyopadhyay, D. Bhattacharya and S. Basu, *J. Phys. Chem. A*, 2001, **105**, 9077.
9 J. A. Simon, S. L. Curry, R. H. Schmehl, T. R. Schatz, P. Piotrowiak, X. Jin and R. P. Thummel, *J. Am. Chem. Soc.*, 1997, **119**, 11012; G. J. Wilson, A. Launikonis, W. H. F. Sasse and A. W.-H. Mau, *J. Phys. Chem. A*, 1997, **101**, 4860; G. J. Wilson, A. Launikonis, W. H. F. Sasse and A. W.-H. Mau, *J. Phys. Chem. A*, 1998, **102**, 5150.
10 A. Harriman, M. Hissler and R. Ziessel, *Phys. Chem. Chem. Phys.*, 1999, **1**, 4203; T. Soujanya, A. Philippon, S. Leroy, M. Vallier and F. Fages, *J. Phys. Chem. A*, 2000, **104**, 9408.