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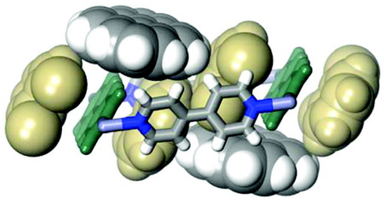

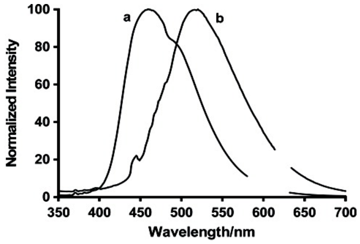

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Exciplex Fluorescence as a Diagnostic Probe of Structure in Coordination Polymers of Zn^{2+} and 4,4′-Bipyridine Containing Intercalated Pyrene and Enclathrated Aromatic Solvent Guests

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Abstract: Coordination polymers based on Zn(II)-4,4′-bipyridine (Zn-bipy) frameworks containing pyrene intercalated between adjacent layers and aromatic solvent molecules enclathrated within the framework cavities have been prepared and characterized for the first time. These compounds are highly fluorescent, and show broad, featureless emission spectra significantly red-shifted relative to pyrene monomer fluorescence; this has been assigned to pyrene-bipy exciplex emission. Single-crystal X-ray structural analysis shows that the presence of the aromatic solvent molecule within the cavities has a profound effect on the architecture of these frameworks: in the case of benzene, toluene, *p*-xylene, and chlorobenzene, the Zn-bipy framework consists of 1-D ladders, whereas in the case of *o*-dichlorobenzene (the largest solvent guest), the framework was based on a 2-D square grid. This difference in stoichiometry and architecture was also reflected in significant differences in the fluorescence of these coordination polymers, with three of the four compounds with 1-D ladder geometries having similar fluorescence maxima (ca. 520 nm) and lifetimes (ca. 70 ns), whereas the compound with square grid topology had a significantly blue-shifted maximum (ca. 460 nm) and shorter lifetime (ca. 42 ns). It is proposed that exciplexes form upon excitation of ground-state complexes, involving face-to-face bipy/pyrene complexes ($\pi-\pi$ stacking interactions) in the case of the 1-D ladder structures, but edge-to-face bipy/pyrene and pyrene/*o*-dichlorobenzene complexes (C−H···π interactions) in the case of the 2-D square grid structure.

Introduction

Coordination polymers have been the subject of a great deal of attention in recent years.[1] To a certain extent this interest is a consequence of the realization that coordination polymers provide chemists with a degree of control over solid-state structure and properties. In a sense, it can be asserted that chemists have discovered how to play a form of molecular Lego[2] in which metal cations represent the bricks (or nodes) and organic ligands represent the glue (or spacers). The “node-and-spacer” approach to self-assembly can be invoked in such a manner that a plethora of infinite architectures[3] and discrete polyhedra[4] can be generated from geometric principles, some of which are unprecedented in either natural or synthetic materials.[5] Coordination polymer nodes are ideally suited for being used as “bricks” for the generation of self-assembled structures for the following reasons: they are invariably based upon previously reported discrete coordination compounds; they

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can be afforded via self-assembly, which typically makes them facile and inexpensive to synthesize, often in one-step with high yield; such structures are inherently modular since they contain at least two components, affording diversity of compositions since both the node and the spacer can be modified without loss of overall topology; open framework structures can be designed from first principles, and the chemist can therefore gain precise control over cavities and channels, making them particularly useful for selective sorption of small molecules;[6] coordination polymers can contain active chromophores in both components;[7] and the presence of guest molecules can invoke functionality or influence the properties of coordination polymers.[8]

In the context of coordination polymers, those that are sustained by 4,4′-bipyridine (bipy) spacers or extended versions of bipy (e.g., 4,4′-(1,2-ethanediyl)bis-pyridine and 4,4′-(1,2-ethenediyl)bis-pyridine) are among the earliest and most widely studied class of coordination polymers.[9] They can be prepared from a wide range of metals, and they exhibit a rich degree of superstructural diversity. For example, bipy has commonly been coordinated to metals in 1:1, 1:1.5, 1:2, and 1:3 metal/ligand ratios; 1:1 stoichiometry can afford molecular polygons or chains (zigzag, linear, or helical); 1:1.5 stoichiometry can form 1-D ladder structures; 1:2 stoichiometry can generate 2-D square grid or 3-D diamondoid topologies; and 1:3 stoichiometry has been shown to produce a 3-D cubic framework (Figure 1).

Previously, we reported the use of pyrene, a well studied[10] highly polarity-sensitive fluorescent probe as a guest molecule to study the environment within metal-bipy coordination polymers and to investigate how large aromatic guests can influence the topology and/or crystal packing of coordination polymers.[11] Resulting from the well-known ability of transition-metal cations to quench the fluorescence emission of aromatic hydrocarbons the metal cation chosen for these studies was Zn(II) as it possesses a d^{10} electronic configuration and therefore does not significantly quench the fluorescence emission of pyrene.

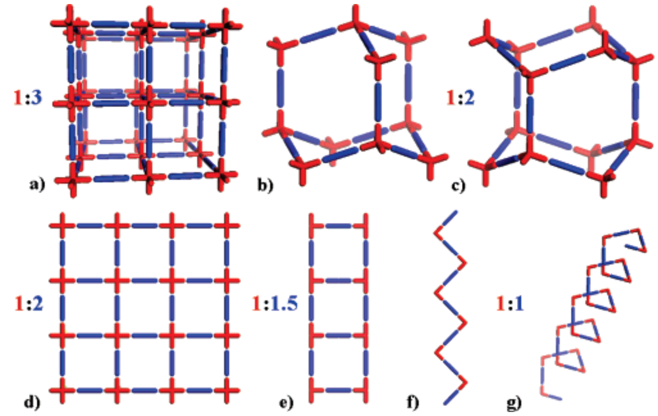

Figure 1. Schematic representation for using metal “nodes” (red) and organic “spacers” (blue) to construct 1-D, 2-D, and 3-D metal−organic networks: (a) cubic; (b) cubic diamond; (c) hexagonal diamond; (d) square grid; (e) ladder; (f) zigzag; (g) helix.

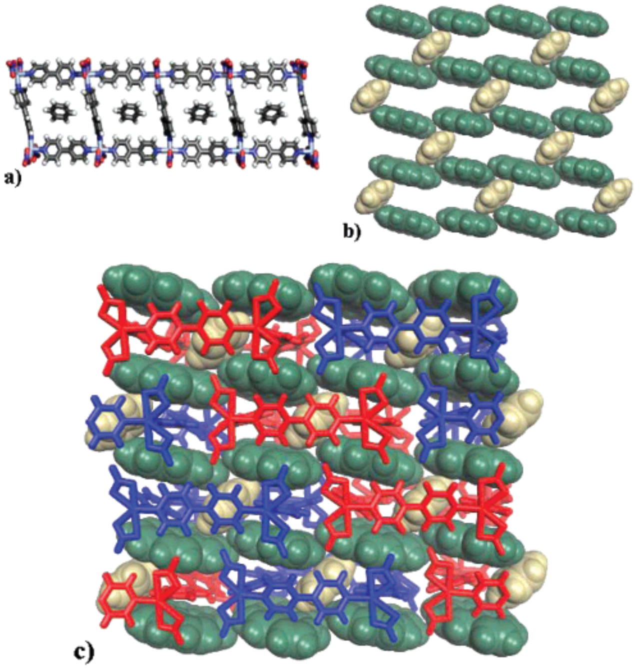

Figure 2. Crystal structure of **1**, the Zn-bipy-pyrene-benzene coordination polymer, illustrating: (a) the 1-D Zn-bipy ladder coordination polymer and the single benzene included in each cavity; (b) the 2-D $[(\text{benzene})/(\text{pyrene})_2]_n$ noncovalent network sustained by edge-to-face C−H···π interactions (benzene and pyrene shown in gold and green, respectively); and (c) interpenetration of the noncovalent network as shown in part b and the 1-D Zn-bipy ladders (pictured in red and blue).

In this contribution we have prepared a number of Zn-bipy coordination polymers of 1-D ladder and 2-D square grid topologies containing pyrene guest molecules in addition to other smaller aromatic guest molecules (i.e., benzene, toluene, *p*-xylene, chlorobenzene, and *o*-dichlorobenzene). These structures have been characterized by single-crystal X-ray diffraction and

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Table 1. Crystallographic Data for Compounds **1**−**5**

	1	2	3	4	5
formula	$C_{68}H_{50}N_{10}O_{12}Zn_2$	$C_{69}H_{44}N_{10}O_{12}Zn_2$	$C_{70}H_{54}N_{10}O_{12}Zn_2$	$C_{68}ClH_{49}N_{10}O_{12}Zn_2$	$C_{48}Cl_4H_{34}N_6O_6Zn$
mol wt	1329.92	1335.88	1357.97	1364.36	997.98
color, habit	yellow, plate	yellow, plate	yellow, needle	yellow, parallelepiped	yellow, parallelepiped
cryst syst	triclinic	triclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$
Z	2	2	2	2	4
a (Å)	11.3503(9)	11.3895(11)	11.3718(9)	11.3364(12)	16.5243(17)
b (Å)	15.1148(12)	15.1659(14)	15.1633(12)	15.1363(16)	11.4647(11)
c (Å)	18.0032(14)	17.8768(16)	17.9472(15)	18.0214(19)	22.731(2)
α (deg)	87.766(2)	88.365(2)	88.393(2)	87.884(2)	90
β (deg)	72.397(2)	73.960(2)	73.2150(10)	72.040(2)	99.120(2)
γ (deg)	87.527(2)	87.750(2)	87.949(2)	88.328(2)	90
V (Å^3)	2940.1(4)	2964.9(5)	2960.5(4)	2939.1(5)	4252.8(7)
temp (K)	100(2)	100(2)	100(2)	100(2)	100(2)
ρ_{calcd} (g·cm^{-3})	1.502	1.496	1.523	1.542	1.559
μ (mm^{-1})	0.892	0.885	0.888	0.939	0.890
GOF	1.029	0.916	0.976	0.847	0.806
θ range	1.19−28.28°	1.19−28.30°	1.19−28.26°	1.19−25.05°	1.81−25.00°
reflns collected	17994	18018	18083	14129	8253
independent reflns (R_{int})	13005 (0.0263)	13059 (0.0340)	13118 (0.0236)	10177 (0.0168)	3700 (0.0204)
$R(F)$, $R_w(F)$	0.0435, 0.0956	0.0558, 0.1434	0.0418, 0.1035	0.0386, 0.1025	0.0338, 0.0940

their intrinsic host/guest interactions have been studied in the solid-state via time-resolved and steady-state fluorescence spectroscopy. Herein we report some insight upon the influence of the network environment upon the fluorescence properties of pyrene and of the pyrene molecules upon the crystal packing of the coordination polymers. (See Table 1 for crystallographic data.)

Results and Discussion

Compounds **1**−**4** form isostructural 1-D ladder coordination polymers, $[Zn(bipy)_{1.5}(NO_3)_2]_n$, with pyrene intercalated between adjacent ladders and an aromatic solvent molecule (**1** = benzene, **2** = toluene, **3** = *p*-xylene, **4** = chlorobenzene) located in the cavity of the $[Zn(bipy)_{1.5}(NO_3)_2]_n$ ladders (Figure 2a). Each Zn(II) cation in **1**−**4** is coordinated to three bipyridine ligands (Zn−N bond distances: 2.107−2.168 Å) and two bidentate nitrate anions (Zn−O bond distances: 2.180−2.498 Å) which generates an overall neutral framework. Although the coordination sphere appears to be seven coordinate, it may be regarded as possessing a trigonal bipyramidal geometry if the nitrates are assumed to occupy only one coordination site each. These distances are expected since statistically identical distances have been observed in the related discrete complex $[Co(pyridine)_3(NO_3)_2]$.[12] In compounds **1**−**4** the torsion angle between the planes of the pyridyl rings in the bipy ligands lies within the range of 23.98°−31.66°; such values are consistent with the bimodal distribution of torsion angles exhibited by crystal structures that contain bipy bridging two metals in the Cambridge Structural Database (CSD).[13a,b] The 1-D ladders propagate along the *a*-axis and stack next to each other along the *c*-axis forming 2-D sheets of parallel ladders which are held together through weak C−H···O hydrogen bonds (range of bond distances measured between the C and O atoms and angles in **1**−**4**: 3.005−3.295 Å; 108.3°−126.6°) between the bipys and the nitrates of adjacent ladders. These distances and angles are well within the normal ranges for C−H···O hydrogen bonds.[14] Along the *b*-axis the 2-D sheets of ladders pack in an ABAB fashion with pyrene intercalated between the layers. The guest molecules interact through arene/pyrene edge-to-face C−H···π stacking to form a 2-D noncovalent sheet as shown for compound **1** in Figure 2b (bond distances measured from the arene carbon in addition to the methyl carbons in compounds **2** and **3** to the mean plane of the pyrene range from 3.429 to 3.740 Å); these distances are within expected values for C−H···π interactions.[15] The noncovalent array can be interpreted as a (6:3) network if it is assumed the node of the network is the center of gravity between adjacent pyrene molecules and a neighboring aromatic solvent molecule. The interpenetration observed between the $[(arene)/(pyrene)_2]_n$ noncovalent sheets and the Zn-bipy 1-D ladders can best be described as parallel/parallel inclined interpenetration (Figure 2c).[9g] The pyrene molecules interact with the bipy ligands oriented parallel to the *a*-axis through face-to-face $\pi-\pi$ stacking to form an infinite array of $\pi-\pi$ stacked bipy/pyrene along the *b*-axis (Figure 3). In compounds **1**−**4** the distances between the centroids of the bipy moieties and the mean plane of the pyrene molecules are between 3.46 and 3.63 Å; which would be expected for $\pi-\pi$ interactions.[16] These results are strikingly different than our previous report of a Zn-bipy ladder and pyrene which resulted in a discrete 2:1 bipy/pyrene complex.[11] Synthetically the only discernible difference between this previous example and the compounds presented herein are the presence of other aromatic

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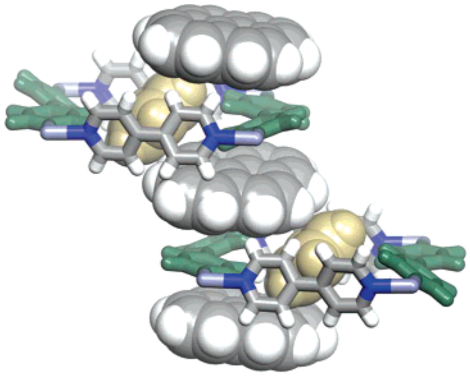

Figure 3. Face-to-face bipy/pyrene $\pi\cdots\pi$ stacking interactions in **1**. Bipy ligands which interact with pyrene are highlighted in green. Benzene guest molecules are shown in gold for clarity and interact with pyrene and bipy ligands through $C-H\cdots\pi$ interactions (nitrate anions have been omitted for clarity).

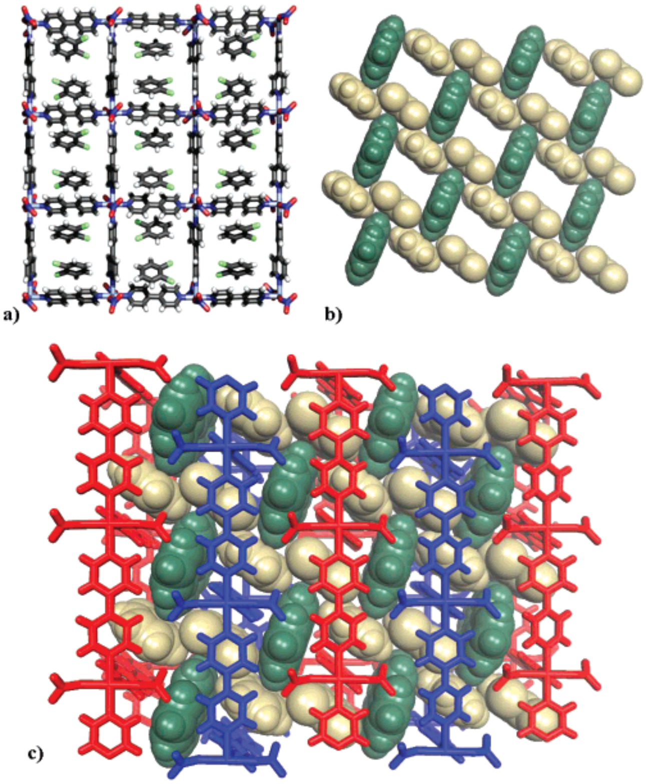

Figure 4. Crystal structure of **5**, the Zn-bipy-pyrene-*o*-DCB coordination polymer, illustrating (a) the 2-D square grid coordination polymer and the two *o*-DCB included in each cavity; (b) the 2-D $[(o\text{-DCB})_2/(\text{pyrene})]_n$ noncovalent network sustained by edge-to-face $C-H\cdots\pi$ interactions (*o*-DCB and pyrene shown in gold and green, respectively); and (c) interpenetration of the noncovalent network as shown in part b and the Zn-bipy square grids (pictured in red and blue).

benzene-like solvents in **1**−**4**. The actual influence the aromatic solvents have on generating **1**−**4** is currently unknown, moreover the reaction and nucleation mechanisms of most coordination polymers are currently poorly understood.

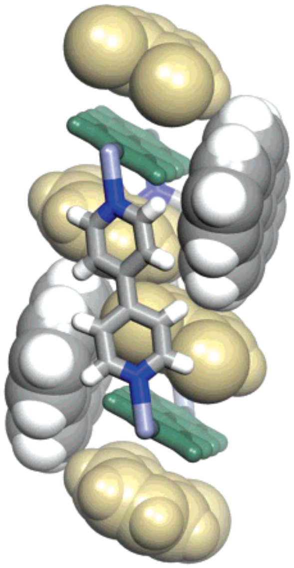

Figure 5. Edge-to-face bipy/pyrene $C-H\cdots\pi$ interactions in **5**. Bipy ligands which interact with pyrene are highlighted in green. *o*-DCB guest molecules are shown in gold for clarity and interact with pyrene through $C-H\cdots\pi$ interactions and bipy ligands through $\pi-\pi$ stacking and $C-H\cdots\pi$ interactions (nitrate anions have been omitted for clarity).

Compound **5** forms a 2-D square grid coordination polymer, $[\text{Zn(bipy)}_2(\text{NO}_3)_2]_n$, with pyrene intercalated between the 2-D sheets and two *o*-dichlorobenzene (*o*-DCB) molecules located in each of the square cavities (Figure 4a). The Zn(II) cations in **5** possess an octahedral geometry coordinated by four bipyridine ligands (Zn−N bond distances: 2.129 − 2.200 Å) and two monodentate nitrate anions (Zn−O bond distance: 2.165 Å) generating an overall neutral framework. Crystallographically there are two unique bipy ligands in compound **5** with torsion angles of 0.0° and 27.442° between the pyridyl rings.[13b,c] The 2-D square grids exhibit a type C packing (as described in reference 9g) with an interlayer separation of 8.164 Å and pyrene intercalated between the layers. The layers also interact through weak $C-H\cdots O$ hydrogen bonds (bond distances measured between the C and O atoms and angles: 3.165 Å; 148.8°) between the bipy's and the nitrates of adjacent 2-D layers. The square cavities are large enough (Zn−Zn bond distances: 11.374−11.472 Å) to accommodate two *o*-DCB molecules which interact with the planar bipy ligands through face-to-face $\pi-\pi$ stacking to form a 2:1 *o*-DCB/bipy sandwich complex (Figure 5); the distance between the centroid of the bipy moiety and the mean plane of the *o*-DCB molecule is 3.418 Å. The guest molecules interact through pyrene/*o*-DCB edge-to-face $C-H\cdots\pi$ stacking to form a 2-D noncovalent sheet as shown in Figure 4b (bond distances measured from the pyrene carbon to the mean plane of the *o*-DCB: 3.541 Å); this distance is within expected values for $C-H\cdots\pi$ interactions.[14] The noncovalent array can be interpreted as a (6:3) network if it is assumed the node of the network is the midpoint of this pyrene/*o*-DCB $C-H\cdots\pi$ bond. The interpenetration observed between the $[(o\text{-DCB})_2/(\text{pyrene})]_n$ noncovalent sheets and the $[\text{Zn(bipy)}_2(\text{NO}_3)_2]_n$ square grids can also be described as the parallel/parallel inclined interpenetration (Figure 4c). The pyrene molecules interact with the planar bipy ligands through bipy/pyrene edge-to-face $C-H\cdots\pi$ stacking (bond distances measured from the bipy carbon to the mean plane of the pyrene: 3.669−3.712 Å); these distances are expected for $C-H\cdots\pi$ interactions.[15]

Fluorescence Spectroscopy. As discussed in our initial paper on the Zn-bipy-pyrene coordination polymer in the absence of aromatic solvent guest, two fluorescence bands can be observed from these compounds. One of these, in the 350−425 nm region, is clearly assignable to pyrene monomer emission, while the other, in the 400−700 nm region, is assigned to 2:1 pyrene/

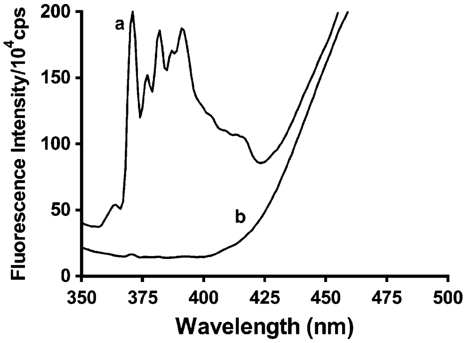

Figure 6. Emission spectrum of the Zn-bipy-pyrene coordination polymer (excitation wavelength 310 nm, emission shown in the monomer emission region): (a) freshly crushed and repeatedly UV-exposed and (b) powder prepared several months prior to measurement of spectrum.

bipy exciplex emission.[11] We now have evidence that this observed monomer emission arises from pyrene adsorbed to the surface of the coordination polymer surface and that the pyrene intercalated within the layers of this coordination polymer gives rise solely to exciplex emission. Emission spectra collected using samples synthesized many months previously showed no evidence of monomer emission. However, if these same samples were freshly crushed, then the monomer emission is clearly observed. Increased monomer emission could also be observed by leaving the sample in the fluorimeter for several hours, exposed to the 320 nm excitation light. This is clearly illustrated in Figure 6, which shows an expanded monomer region and compares the results obtained for a previously prepared sample used as is and freshly crushed and exposed to UV. We hypothesize that freshly prepared samples of this coordination polymer contain significant amounts of pyrene monomers adsorbed to the surface, which disappear through sublimation over a period of time. Crushing a sample releases more pyrene molecules, which again adsorb to the surface. Continued exposure to UV light also must break down the coordination polymer structure to some degree, again releasing pyrene monomers. Thus, only the observed exciplex band can be used to characterize the coordination polymer; the I_{III}/I_{I} vibronic band ratio of the observed monomer[17] cannot be used to determine the polarity of the local environment of the pyrene intercalated within the coordination polymer, as was previously reported.

Strong fluorescence emission was observed from all five of the Zn-bipy-pyrene coordination polymers with aromatic solvent guests (weak monomer bands of varying intensities relative to the exciplex bands were also observed and assigned as discussed above). Figure 7 shows the emission spectra for compounds **2** and **5**, namely those with toluene and *o*-DCB as guests. Table 2 lists the observed fluorescence maxima for compounds **1**−**5**, for four (or in two cases five) different synthesis trials.

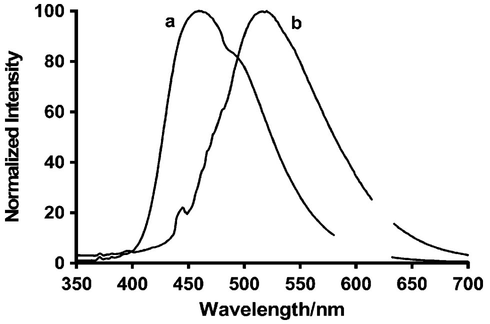

Figure 7. Emission spectrum of the Zn-bipy-pyrene coordination polymers (excitation wavelength 310 nm): (a) **5** (*o*-DCB) and (b) **2** (toluene).

Table 2. Fluorescence Emission Wavelength Maxima ($\lambda_{F,max}$, in nm) for the Zn-bipy-pyrene Coordination Polymers with Aromatic Solvent Guests

aromatic guest	trial no. 1	trial no. 2	trial no. 3	trial no. 4	trial no. 5	average
1−benzene	513	456	477	476/505	505	
2−toluene	517	519	515	517		517 ± 2
3−*p*-xylene	520	520	475	522	521	521 ± 1[a]
4−CB	525	525	519	522		523 ± 3
5− *o*-DCB	460	461	458/509	457		459 ± 2[b]

[a] Trial 3 excluded. [b] Second value for trial 3 excluded.

Table 3. Fluorescence Lifetimes (τ_F, in ns) of the Zn-bipy-pyrene Coordination Polymers with Aromatic Solvent Guests

aromatic guest	trial no. 1	trial no. 2	trial no. 3	trial no. 4	trial no. 5	avg
1−benzene	72	28/41	42	51/61	78	
2−toluene	71	75	70	80		74 ± 5
3−*p*-xylene	76	74	22[a] 46	87	71	77 ± 7[b]
4−CB	73	73	68	75		72 ± 3
5−*o*-DCB	42	42	44/68	44		43 ± 1[c]

[a] Calculated using a 2-exp fit. [b] Trial 3 excluded. [c] Second value for trial 3 excluded.

In the cases of compounds **2** (toluene) and **4** (chlorobenzene), excellent consistency was obtained, with $\lambda_{F,max}$ values of 517 ± 2 and 523 ± 3 nm, respectively. These values are slightly blue-shifted compared to that of 540 nm obtained for the original Zn-bipy-pyrene coordination polymer (i.e., with included methanol solvent). In the case of compound **3** (*p*-xylene), four of the five samples gave similar results, with an average $\lambda_{F,max}$ of 521 ± 1 nm, consistent with the results of **2** and **4**. One trial, however, gave a significantly blue-shifted spectrum, with a $\lambda_{F,max}$ of 475 nm, suggesting perhaps a different structure. In the case of compound **5** (*o*-DCB), a significantly blue-shifted exciplex emission was observed, with a $\lambda_{F,max}$ of 459 ± 2 nm. In one trial, a second type of crystal was observed, which appeared darker, and which gave a different fluorescence maximum of 509 nm (similar to that for **2** and **4**). In the case of compound **1** (benzene), great inconsistencies were observed, with some trials showing $\lambda_{F,max}$ values above 500 nm (similar to **2** and **4**) and others showing values around 460 nm (similar to **5**) and one trial showing two types of crystals, one of each type.

Similar results were obtained for the fluorescence lifetimes τ_F, as shown in Table 3. In one case (trial #3 with **3**), a two-exponential decay curve was required to fit the data; however, in all other cases the decay curves fit well to a single-exponential function. Compounds **1**, **3**, and **4** (with the exception of one trial) all had τ_F on the order of 74 ns, whereas compound **5** (*o*-DCB) had a much shorter τ_F of 43 ns. Although it is possible that this significant decrease in lifetime was caused by the external heavy atom effect[18] of the two chlorines on this solvent, no decrease of any size is observed in compound **4** (chlorobenzene). We therefore conclude that it must be a result of a difference in structure. Again, compound **1** (benzene) showed

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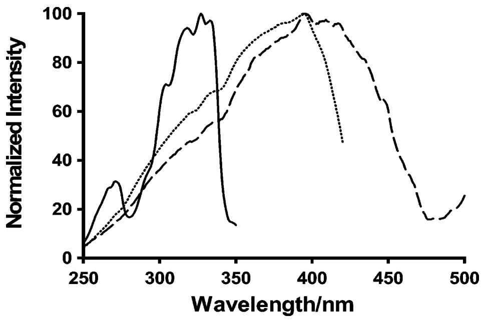

Figure 8. Excitation spectra of pyrene in methanol [—] and the Zn-bipy-pyrene coordination polymers **5** (*o*-DCB) [···] and **2** (toluene) [---] as guests. The emission wavelengths monitored were 380, 430, and 502 nm, respectively.

great inconsistencies, with some trials giving compounds with τ_F in the range of 72−78 ns and others around 42 ns.

These fluorescence results are consistent with the structural results described in the previous section, namely, that coordination polymers **1**−**4** containing benzene, toluene, *p*-xylene, and chlorobenzene all exhibit 1-D ladder architectures, while **5** with *o*-DCB exhibits a 2-D square grid architecture. This difference in structure is clearly manifested in the fluorescence results, with the 1-D ladder structures having $\lambda_{F,max}$ values around 520 nm and τ_F values around 74 ns, whereas the square grid structures have $\lambda_{F,max}$ values around 460 nm and τ_F values around 43 ns. This is very significant, as it illustrates that the exciplex emission can be used diagnostically to indicate the type of architecture obtained in these coordination polymers, with distinctive fluorescence maxima and lifetimes observed for these two very different structures. The variable results from trial to trial observed in the case of **1**, which showed maxima and lifetimes in both ranges, suggest that for this solvent, both architectures are possible. Thus, the formation of these two structures in this particular case must be very similar in terms of both kinetics and thermodynamics, and which structure is obtained in a given trial must depend on slight variations in experimental conditions, such as concentrations of all the components and the aromatic solvent/methanol ratio. This was also observed, to a much lesser extent, in the case of **3** (*p*-xylene), which gave results consistent with a square grid structure in one of the five trials, and in the case of **5** (*o*-DCB), which gave results consistent with both square grid and 1-D ladder structures in one trial (but not in the other three trials).

The nature of the pyrene emission observed can be further investigated by comparing the excitation spectrum of these compounds to that of pyrene in solution; this yields information about the nature of the emitting state. These excitation spectra are shown in Figure 8. Whereas the excitation spectrum of pyrene in methanol solution reproduces very nicely the absorption spectrum (not shown), that of compounds **2** (toluene) and **5** (*o*-DCB) are clearly red-shifted and relatively broad and featureless, indicative of the formation of a ground-state charge-transfer complex. This shows that pyrene is complexed in these compounds even in the ground state and that the exciplex is formed by direct excitation of this complex and not by the solution mechanism of excitation of a monomer followed by complexation of the excited-state species with a ground-state species. Furthermore, the excitation spectrum of **2** (toluene) is significantly more red-shifted than **5** (*o*-DCB), supporting our proposal on the difference in the nature of the pyrene complexation in the 1-D ladders versus 2-D square grid structures. Excitation of such a ground-state charge-transfer complex could potentially lead to photoinduced electron transfer in these compounds.

In the case of the 1-D ladders in **1**−**4**, the observed exciplex emission can be assigned to an infinite array of bipy/pyrene exciplexes, which differs from our previous report of a Zn-bipy ladder and pyrene which resulted in a discrete 2:1 bipy/pyrene complex.[11] In contrast, the present 1-D ladders have a net bipy/pyrene ratio of 1:1, and it is interesting to note that in this case the pyrene emission is not as strongly red-shifted (520 nm) as was the case in those previously reported 2:1 exciplexes (540 nm). Figure 3 clearly shows how the pyrene and bipy are π-stacked on top of each other and thus how an exciplex can form upon excitation of the pyrene fluorophore. This is an ideal arrangement to maximize the $\pi-\pi$ interactions;[15] this then leads to exciplex formation upon excitation of the ground state pyrene in the bipy/pyrene complex, in an analogous way to a previous report of excimer/exciplex formation upon excitation of van der Waals dimers of aromatic molecules.[19] This mechanism also precludes the observation of monomer emission from these structures, since every pyrene is complexed. The observed emission maximum of ca. 520 nm compares well to that of other reported pyrene exciplexes, including a 1:1 dimethylaniline/pyrene exciplex with a reported emission maximum of 496 nm[20] and with a reported 2:1 4,4′-bis(dimethylamino)diphenylmethane triplex, which had an emission maximum of 590 nm.[21] Furthermore, there have been cases of the formation of exciplexes between bipy and other fluorescent probes reported, for example that between bipy and a phenanthroline-based macrocycle in a rotaxane structure.[22]

In the case of the **5** (*o*-DCB) square grid, however, a different assignment of the observed 460 nm emission is required. As can be seen from Figure 5, there is no face-to-face interaction of pyrene with any of the aromatic moieties in this structure, including bipy, *o*-DCB, or neighboring pyrenes. In this case, the red-shifted emission observed may be the result of a T-shaped exciplex, in which the bipy hydrogens interact with the pyrene π-electrons in an edge-to-face manner, that is, a $C-H\cdots\pi$ interaction. This possibility is clearly shown in Figure 5; bond distances measured from the bipy carbon to the mean plane of the pyrene range from 3.669 to 3.712 Å but are well within expected distances for $C-H\cdots\pi$ interactions.[16] This interaction can be considered a very weak hydrogen bond and would be expected to be a much weaker interaction than $\pi-\pi$ stacking, and this is consistent with the significantly smaller degree of red-shifting of the pyrene emission observed in this case: 460 versus 520 nm. There have been numerous examples of such edge-to-face $C-H\cdots\pi$ interactions between aromatic species reported in the recent literature.[23] In fact, a critical survey of π-interactions in metal complexes with aromatic ligands containing nitrogen concludes that in only a limited number of cases does near perfect face-to-face alignment occur and that in many reported structures the interaction in fact occurs through

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off-set face-to-face or edge-to-face interactions.[24] As shown in Figure 5 these *o*-DCB solvent molecules in the cavity also interact with pyrene, in a similar way as bipy as described above, through pyrene/*o*-DCB edge-to-face C−H···π stacking (bond distances measured from the pyrene carbon to the mean plane of the *o*-DCB are 3.541 Å). It is this combination of bipy and *o*-DCB edge-to-face stacking with pyrene that results in the observed red-shifted pyrene emission. This is a very complex and unique pyrene emitting state. Furthering this complicated electronic structure, the *o*-DCB molecules also interact with the planar bipy ligands through face-to-face $\pi-\pi$ stacking, forming 2:1 *o*-DCB/bipy sandwich complexes (Figure 5); the distance between the centroid of the bipy moiety and the mean plane of the *o*-DCB molecule is 3.418 Å. As noted above, the net effect of all of these edge to face interactions on the pyrene is significantly less than that of the face to face interactions with bipy observed in the 1D ladder structures.

Conclusions

A series of fluorescent Zn-bipy coordination polymers have been prepared with pyrene intercalated between the layers and aromatic solvent molecules incorporated within the cavities defined by the Zn-bipy coordination. The type of structure obtained depends on the nature of the enclathrated solvent molecule: in the case of benzene, toluene, *p*-xylene, and chlorobenzene, a 1-D ladder architecture was obtained, whereas in the case of *o*-DCB, a 2-D square grid architecture was obtained. The fluorescence of these compounds is diagnostic of the structure: the 1-D ladder compounds had fluorescence maxima around 520 nm and fluorescence lifetimes around 70 ns, whereas the square grid compounds had fluorescence maxima around 460 nm and fluorescence lifetimes around 40 ns. In the case of benzene, the fluorescence of various samples varied between these two sets of values, suggesting that either type of structure can be obtained in this case. In the case of the 1-D ladder structures, the emission is easily assignable to an extended 1:1 bipy/pyrene exciplex network, which results from direct excitation of the corresponding ground-state complex. In the case of the 2-D square grid structures, face-to-face interaction of pyrene with a second aromatic species does not occur, so the observed red-shifted emission is assigned to exciplex formation resulting from direct excitation of pyrene interacting with the hydrogens along the bipy and *o*-DCB edges. The edge-to-face interactions in the 2-D square grid structures results in significantly lower red-shifting of the pyrene exciplex emission as compared to the face-to-face interactions in the 1-D ladder structures.

Experimental Section

All materials were used as received; solvents were purified and dried according to standard methods.

Synthesis of {[Zn(bipy)$_{1.5}$(NO$_3$)$_2$]·1/2 benzene·pyrene}$_n$ (1). Light yellow-brown crystals of **1** were obtained from slow diffusion via layering a methanol solution (15.0 mL) of zinc nitrate hexahydrate (147 mg, 0.49 mmol) onto a methanol solution (10.0 mL) of 4,4′-bipyridine (156 mg, 1.0 mmol), pyrene (405 mg, 2.0 mmol), and benzene (5.0 mL, 56 mmol) in a 40 mL vial, which was subsequently capped and allowed to remain undisturbed at room temperature until diffusion was completed. Crystals began to form within hours and growth was completed after one week. The crystals were harvested and dried via vacuum filtration yielding 147 mg (44%) of **1**.

Synthesis of {[Zn(bipy)$_{1.5}$(NO$_3$)$_2$]·1/2 toluene·pyrene}$_n$ (2). Light yellow-brown crystals of **2** were obtained from slow diffusion via layering a methanol solution (15.0 mL) of zinc nitrate hexahydrate (148 mg, 0.50 mmol) onto a methanol solution (10.0 mL) of 4,4′-bipyridine (156 mg, 1.0 mmol), pyrene (404 mg, 2.0 mmol), and toluene (5.0 mL, 47 mmol) in a 40 mL vial, which was subsequently capped and allowed to remain undisturbed at room temperature until diffusion was completed. Crystals began to form within hours and growth was completed after one week. The crystals were harvested and dried via vacuum filtration yielding 118 mg (35%) of **2**.

Synthesis of {[Zn(bipy)$_{1.5}$(NO$_3$)$_2$]·1/2 *p*-xylene·pyrene}$_n$ (3). Light yellow-brown crystals of **3** were obtained from slow diffusion via layering a methanol solution (15.0 mL) of zinc nitrate hexahydrate (147 mg, 0.49 mmol) onto a methanol solution (10.0 mL) of 4,4′-bipyridine (154 mg, 0.99 mmol), pyrene (406 mg, 2.0 mmol), and *p*-xylene (5.0 mL, 40 mmol) in a 40 mL vial, which was subsequently capped and allowed to remain undisturbed at room temperature until diffusion was completed. Crystals began to form within hours and growth was completed after one week. The crystals were harvested and dried via vacuum filtration yielding 190 mg (56%) of **3**.

Synthesis of {[Zn(bipy)$_{1.5}$(NO$_3$)$_2$]·1/2 chlorobenzene·pyrene}$_n$ (4). Light yellow-brown crystals of **4** were obtained from slow diffusion via layering a methanol solution (15.0 mL) of zinc nitrate hexahydrate (148 mg, 0.50 mmol) onto a methanol solution (10.0 mL) of 4,4′-bipyridine (157 mg, 1.01 mmol), pyrene (407 mg, 2.01 mmol), and chlorobenzene (5.0 mL, 49 mmol) in a 40 mL vial, which was subsequently capped and allowed to remain undisturbed at room temperature until diffusion was completed. Crystals began to form within hours and growth was completed after one week. The crystals were harvested and dried via vacuum filtration yielding 174 mg (51%) of **4**.

Synthesis of {[Zn(bipy)$_2$(NO$_3$)$_2$]·2 *o*-dichlorobenzene·pyrene}$_n$ (5). Light yellow-brown crystals of **5** were obtained from slow diffusion via layering a methanol solution (15.0 mL) of zinc nitrate hexahydrate (146 mg, 0.49 mmol) onto a methanol solution (10.0 mL) of 4,4′-bipyridine (157 mg, 1.01 mmol), pyrene (403 mg, 1.99 mmol), and *o*-dichlorobenzene (5.0 mL, 44 mmol) in a 40 mL vial, which was subsequently capped and allowed to remain undisturbed at room temperature until diffusion was completed. Crystals began to form within hours and growth was completed after one week. The crystals were harvested and dried via vacuum filtration yielding 212 mg (42%) of **5**.

X-ray Crystallography. Single crystals suitable for X-ray crystallographic analysis were selected following examination under a microscope. Intensity data were collected on a Bruker-AXS SMART APEX/CCD diffractometer using Mo Kα radiation ($\lambda = 0.7107$ Å).[25] The data were corrected for Lorentz and polarization effects and for absorption using the SADABS program (SAINT).[26] The structures were solved using direct methods and refined by full-matrix least-squares on $|F|^2$ (SHELXTL).[27] All non-hydrogen atoms were refined anisotropically. The sp^3 methyl hydrogens atoms in **3** were located and given a thermal parameter of 1.5 times that of the atoms to which they are

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bonded. The other hydrogen atoms were placed in geometrically calculated positions and refined with temperature factors 1.2 times those of their bonded atoms.

Fluorescence Spectroscopy. All fluorescence measurements were performed using a front-face solid sample emission configuration. Powdered samples were adhered to a 45° aluminum support (the base of which was a 1 × 1 cm square to fit a standard spectrometer cuvette holder), using double-sided adhesive tape. Fluorescence spectra were measured on a Photon Technologies International LS-100 luminescence spectrometer, with excitation and emission monochromator bandpasses set at 3 nm and an excitation wavelength of 310 nm (at this wavelength, only pyrene absorbs the excitation light: neither bipy nor any of the benzene-derived guests absorb at 310 nm). Excitation spectra were recorded using the same condition, with the emission wavelength set at an appropriate wavelength based on the corresponding emission spectrum. Time-resolved fluorescence was measured on the same samples using a Photon Technologies International Timemaster fluorescence lifetime spectrometer. This instrument measures fluorescence decay curves using the stroboscopic technique;[28] resulting decay curves were fit to one-or two-exponential decay functions using supplied deconvolution software. Excellent fits were obtained, as indicated by the very good χ^2 statistical test values obtained (which should be close to 1 for a good fit result): an average χ^2 value of 1.11 for the five samples in trial 1 and an overall average of 1.27 for all trials.

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Supporting Information Available: X-ray crystallographic information in CIF format; FTIR, TGA, and PXRD. This material is available free of charge via the Internet at http://pubs.acs.org.

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