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Selective formation of integrated stacks of (α-diimine)-(ethylenediamine)platinum(II) and neutral π systems of the phenanthrene type †

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The $[Pt(en)(L)]^{2+}$ (L = bipy or phen) complexes with a planar α-diimine ligand and a non-planar diamine ligand formed 1 : 1 integrated stacks taking up free phen and phenanthrene (phe) selectively. The stacking structures of the composite crystals $[Pt(en)(L)][PF_6]_2\cdot phen\cdot 2H_2O$ (L = bipy or phen) and $[Pt(en)(bipy)][PF_6]_2\cdot phe$ have been elucidated by X-ray analysis. Both π–π interactions and hydrogen bonds lead to easy and selective uptake of phen to form the integrated stack while it is possible for phe with no hydrogen bonding ability to form a similar integrated stack. The composite crystals exhibit emission spectra which originate from the $^3\pi\pi^*$(L) state of $[Pt(en)(L)]^{2+}$ in the integrated stack. The emission properties indicate facile energy transfer from free phen or phe to $[Pt(en)(L)]^{2+}$ in the stacks.

Introduction

Square-planar platinum(II) complexes containing α-diimine ligands form various stacking structures controlled by metal–metal and ligand π–π interactions in the solid state, which leads to characteristic luminescence properties. For example, two crystal forms, red and yellow, are known for $[PtCl_2(bipy)]$. The red form has a stacked structure with Pt···Pt interaction and emits intense luminescence from the ^{3}MLCT state at room temperature.[1] On the other hand, the yellow form has a π–π stack, and exhibits only weak luminescence based on the d–d transition at low temperature.[2] For $[Pt(CN)_2(i\text{-biq})]$ (*i*-biq = 3,3′-biisoquinoline) containing a more extended π system than bipy, the competition between Pt···Pt and π–π interactions induces a remarkable temperature change of the luminescence.[3] When a non-planar ligand such as ethylenediamine (en) is included with an α-diimine ligand, however, the complex is unfavorable for linear stacking with Pt···Pt interaction because of the steric hindrance of en and the positive charge of the complex. In fact, for $[Pt(bipy)(en)]^{2+}$, the π–π stacking of α-diimines with no particular electronic intermolecular interactions occurs in the solid state.[4] The interplanar spacings of the π–π stacks can be controlled by counter anions that form hydrogen bonds with the en ligand of the complexes. The large anion, PF_6^-, radius roughly estimated to be 2.76 Å, has a role to expand the spacings of the π stack of α-diimine ligands as a pillar. The spacings were found to be 3.60(5) and 3.56(5) Å for $[Pt(en)(phen)][PF_6]_2$, whereas those for $[Pt(en)(phen)]Cl_2$ containing smaller anions[5] were 3.38(1) and 3.40(1) Å.[6] In the course of our studies of α-diimine platinum complexes we have found that the platinum(II) complexes $[Pt(en)(L)]^{2+}$ (L = bipy or phen), take up neutral π-conjugated compounds of the phenanthrene-type selectively, forming 1 : 1 integrated stacks.

Integrated stacks have been reported for some charge-transfer complexes of planar metal complexes and π-conjugated organic compounds.[7] These complexes are constructed by strong donor–acceptor interactions, and exhibit characteristic electrical and magnetic properties. However, those including neutral compounds with little charge-transfer character are not well known. The 1 : 2 crystal $[Pd(tmphen)_2][PF_6]_2\cdot 2bipy$[8] (tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline) and the non-stoichiometric crystal $[Au(phen)(CN)\{(CN)_{0.82}Br_{0.18}\}]\cdot 0.5\textit{trans}\text{-}[Au(CN)_2Br_2]\cdot 0.5Br\cdot phen$[9] are two examples of integrated stacks including bipy or phen. On the other hand, platinum complexes containing aromatic ligands have been paid much attention from the biochemical point of view as probes of DNA and antitumor drugs. Some salts of platinum(II) complexes with DNA fragments and nucleotides form intercalated structures where the base moieties and the platinum complexes stack alternately.[10] In these cases the electrostatic interactions between nucleotides with negative charge and the platinum complexes with positive charge are the main factor for the assemblage, and thus the molecular arrangement due to the weak interactions such as π–π interactions and hydrogen bonds may be restricted by the strong electrostatic interactions. Thus integrated stacks of the inclusion type are very informative in the study of molecular recognition because the molecular arrangement directly reflects the weak intermolecular interactions.

This paper reports the selective uptake of neutral π systems of the phenanthrene type and the structures of the resulting composite crystals of $[Pt(en)(L)][PF_6]_2$ (L = bipy or phen) and phen or phenanthrene as well as evidence for facile energy transfer in the latter based on the luminescence behavior.

Results and discussion

Formation of composite crystals and their structures

The composite crystals, $[Pt(en)(L)][PF_6]_2\cdot phen\cdot 2H_2O$ (L = bipy (**1**) or phen (**2**)) were easily obtained from aqueous solutions

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† Electronic supplementary information (ESI) available: UV-VIS absorption spectra of complexes **1**, **2**, emission spectrum of **2**, stacking diagrams of **2**, **3** and packing diagram of **1**. See http://www.rsc.org/suppdata/dt/b0/b007292n/

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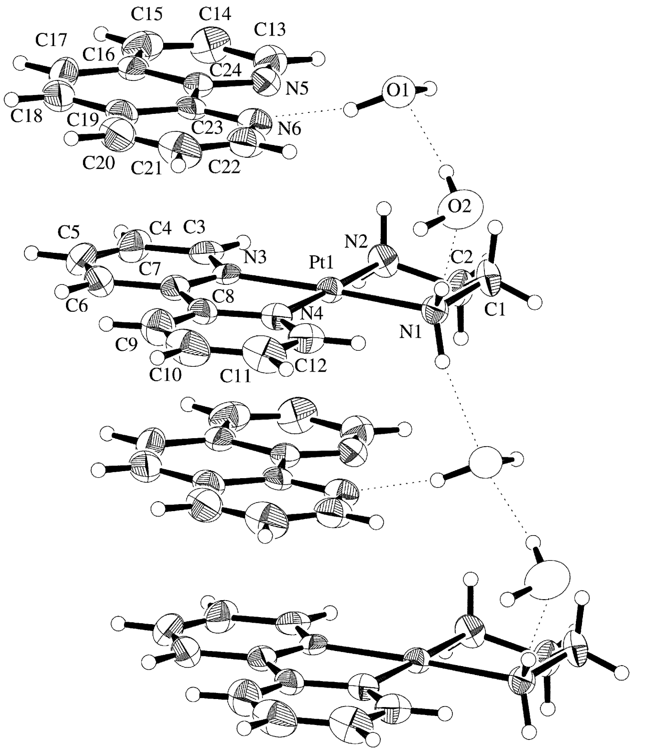

Fig. 1 Perspective view of the integrated stack in the crystal of [Pt(bipy)(en)][PF$_6$]$_2$·phen·2H$_2$O (**1**).

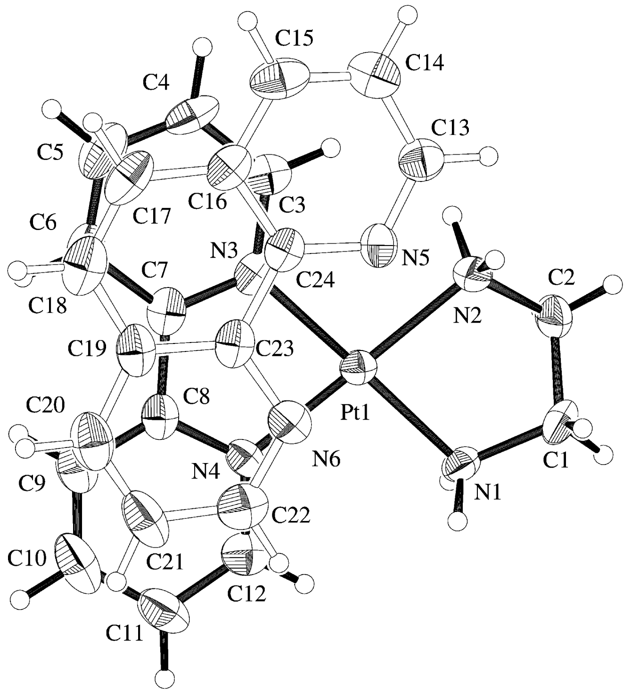

Fig. 2 Top view of the integrated stack in the crystal of [Pt(bipy)(en)][PF$_6$]$_2$·phen·2H$_2$O (**1**).

of the components. Especially, crystal **2** was preferentially obtained also in the preparation of the [Pt(en)(phen)]$^{2+}$ complex under conditions of a slight excess of phen in solution. The 1 : 1 composition of [Pt(en)(L)]$^{2+}$ and free phen was confirmed by means of NMR and UV-VIS spectroscopy (see Experimental section and ESI Figs. S1, S2).

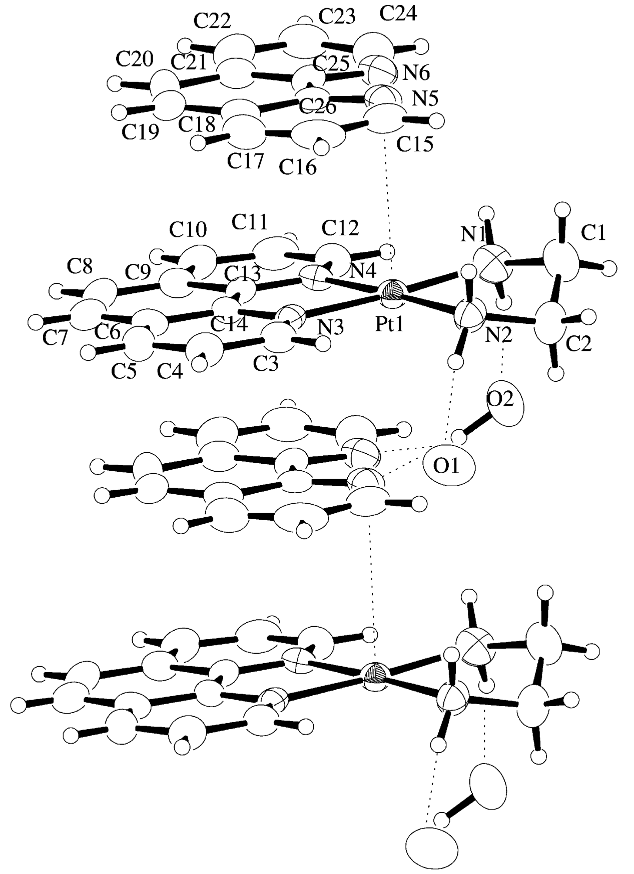

Fig. 3 Perspective view of the integrated stack in the crystal of [Pt(phen)(en)][PF$_6$]$_2$·phen·2H$_2$O (**2**).

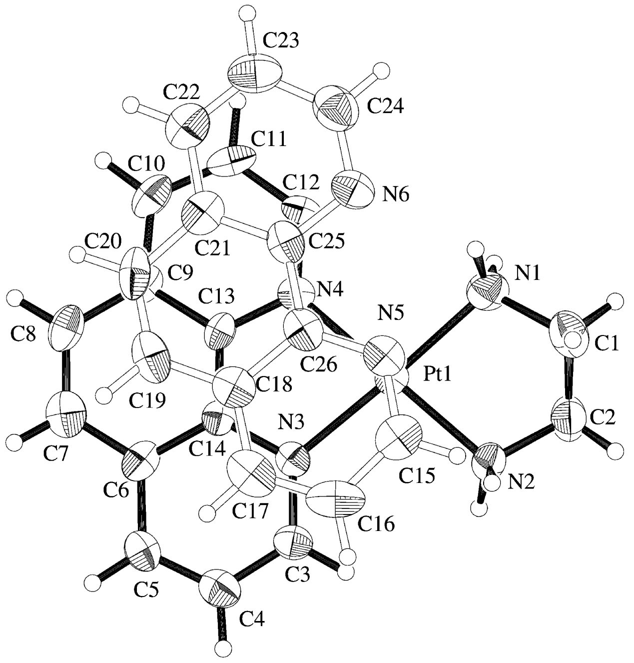

Fig. 4 Top view of the integrated stack in the crystal of [Pt(phen)(en)][PF$_6$]$_2$·phen·2H$_2$O (**2**).

The crystal structures complexes **1** and **2** were determined by X-ray analysis and both found to adopt integrated stacking structures of alternating [Pt(en)(L)]$^{2+}$ and free phen. Figs. 1–4 show the stacking structures, and relevant bond lengths and angles are summarized in Table 1. For **1**, free phen is arranged almost in parallel over the square-planar complex of [Pt(bipy)(en)]$^{2+}$ with interplanar spacings of 3.43(1) and 3.47(1) Å (Fig. 1 and Table 1). These values are typical for efficient π–π stacks. There is a chain of hydrogen bonds through free phen, water molecules and en in the complex (NH$_2$(en) $\cdots$ OH$_2$ $\cdots$ OH$_2$ $\cdots$ N(phen)). The PF$_6^-$ ions also lie on the hydrophilic site linking to en and water molecules by hydrogen bonds though those are omitted in Fig. 1 for clarity (see ESI Fig. S3).

Table 1 Selected bond lengths (Å) and angles (°), and relevant intermolecular contacts and hydrogen bonds

		$[Pt(en)(bipy)][PF_6]_2\cdot phen\cdot 2H_2O$ (**1**)	$[Pt(en)(phen)][PF_6]_2\cdot phen\cdot 2H_2O$ (**2**)	$[Pt(en)(bipy)][PF_6]_2\cdot phe$ (**3**)
	Pt1–N1	2.044(7)	2.05(1)	2.054(9)
	Pt1–N2	2.037(8)	2.034(9)	2.06(1)
	Pt1–N3	2.007(8)	2.029(9)	2.003(8)
	Pt1–N4	2.007(7)	2.022(9)	2.009(9)
	N1–Pt1–N2	82.0(3)	82.7(4)	82.9(4)
	N1–Pt1–N4	98.9(3)	96.9(4)	97.6(4)
	N2–Pt1–N3	98.9(3)	99.6(4)	97.9(4)
	N3–Pt1–N4	80.3(3)	80.8(4)	81.6(4)
π–π spacings		3.43(1) 3.47(1)	3.39(2) 3.45(2)	3.39(2) 3.44(2)
Hydrogen bonds		N1···O1^{i} 3.08(1)	N1···O1 2.87(1)	
		N1···O2^{ii} 2.87(1)	N2···O1 2.88(1)	
		O1···N6 2.74(1)	O2···N5^{ii} 2.90(1)	
		O2···O1^{iii} 2.82(1)	O2···N6^{ii} 3.09(1)	
Special contacts			Pt···N5 3.39(1)	Pt···H17^{i} 3.46

Symmetry codes: (i) $x, y, z - 1$; (ii) $x - 1, y, z$; (iii) $x + 1, y, z$.

Thus both π–π interactions and hydrogen bonds co-operatively stabilize the stack. The importance of both interactions for adduct formation of the platinum complexes and mononucleotides in solution was also pointed out by Odani *et al.*[11] A similar integrated stacking structure is seen also for the crystal of **2** though the hydrogen bonding features are a little different (Fig. 3 and Table 1). In addition, it is interesting for **2** that a nitrogen atom in free phen lies on the axial position of the platinum complex (Pt···N5 3.39(1) Å) as shown in Figs. 3 and 4. The situation is similar to that reported for the integrated stack of $[Cu(qnl)_2]\cdot C_6(NO)_6$ (qnl = quinolin-8-olate ion, $C_6(NO)_6$ = hexanitrosobenzene) with donor–acceptor interactions.[12]

More interestingly, the inclusion of free phen is completely selective. From a solution containing equimolar amounts of $[Pt(en)(L)][PF_6]_2$, phen and bipy, only the composite crystal including phen, $[Pt(en)(L)][PF_6]_2\cdot phen\cdot 2H_2O$, was obtained. Also all trials to make composite crystals of $[Pt(en)(L)][PF_6]_2$ and other small aromatic heterocycles such as bipy, quinoline, phenazine or adenine resulted in failure. In those cases the original complex salts were recrystallized. For compounds with more extended π systems, dipyrido[3,2-*d*:2′,3′-*f*]quinoxaline (dpq) and dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppz), composite crystals with segregated stacks of the platinum complex and those aromatic heterocycles were obtained.[13] Thus the size and shape of the π systems could be the main factor in the selective formation of integrated stacks: Neither smaller nor bigger π systems than phen fit the [Pt(en)(L)] complex and structural isomers of phen with a linear condensed ring such as phenazine and acridine were also excluded. As mentioned above, hydrogen bonds could be another factor for the stabilization of integrated stacks. Compared with bipy, phen is able to build more effective hydrogen bonds through crystal water because of its higher basicity (pK_a = 4.93(4) for phen, 4.42(3) for bipy at 25 °C, 0.1 M ionic strength).[14]

In order to clarify the role of hydrogen bonds in the formation of integrated stacks more precisely, we next investigated the formation of composite crystals using phenanthrene (phe) having with no nitrogen atoms, and obtained crystals of $[Pt(en)(L)][PF_6]_2\cdot phe$ (L = bipy (**3**) or phen (**4**)) from the methanol solution. The structure of **3** was determined by X-ray analysis. As shown in Figs. 5 and 6, the stacking structure for **3** is very similar to that for **1** as well as the crystal lattice in spite of the lack of water molecules. This confirms that hydrogen bonding is not a necessary condition for the formation of composite crystals although it affects the ease of formation. As shown in Fig. 6, the complex and phe adopt an offset geometry so as to realize effective π–π interactions.[15] Interestingly, one hydrogen atom (H17) of phe is found at the apical position of the platinum complex (Pt···H17 3.46 Å, Table 1). The access of a hydrogen atom was found also for the aliphatic macrocyclic complex $[Ni(N_48)]^{2+}$ (N_48 = 1,4,7,10-tetraazacyclopentadecane), where one of the hydrogen atoms of the 8-membered chelate ring is located just above the Ni^{2+} ion at a distance of 2.31(6) Å.[16] This suggests the possibility of M···H interactions which would be a kind of hydrogen bond involving the lone pair electrons in the d orbital.

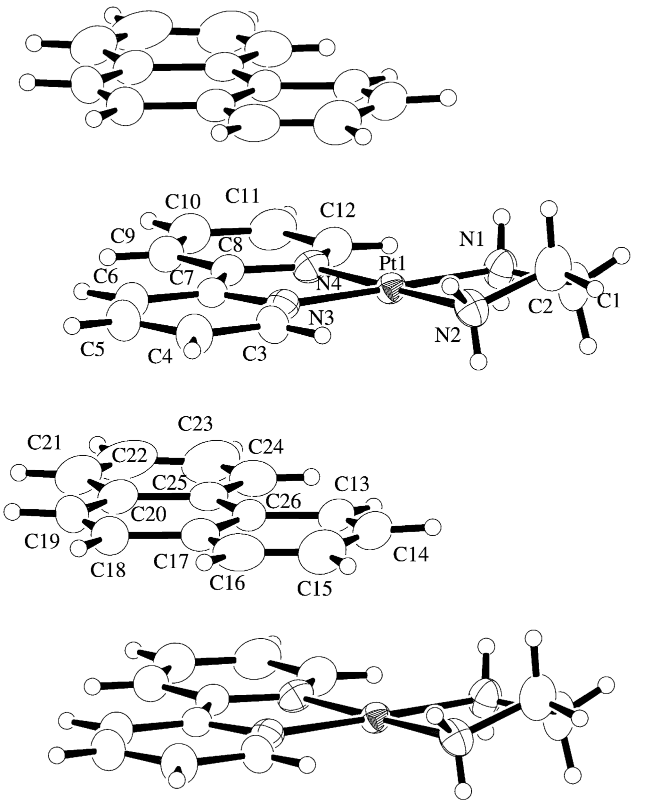

Fig. 5 Perspective view of the integrated stack in the crystal of $[Pt(bipy)(en)][PF_6]_2\cdot phe$ (**3**).

Emission properties of the composite crystals

Fig. 7 shows emission spectra of complex **1** at 77 K. In glassy solution both fluorescence and phosphorescence were observed

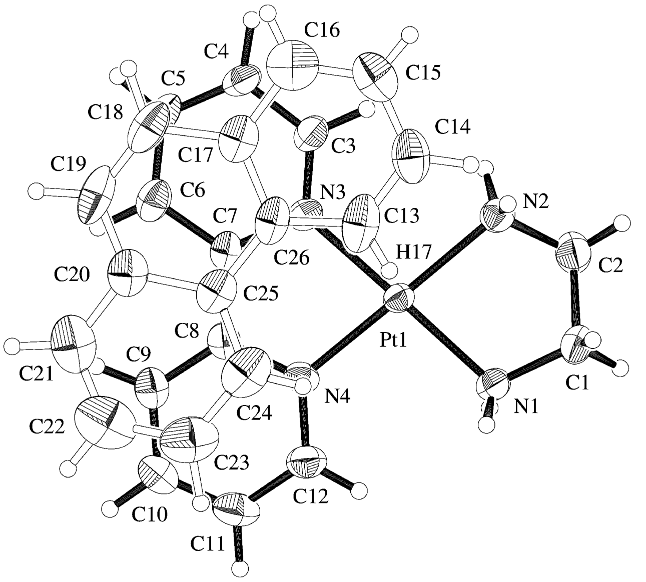

Fig. 6 Top view of the integrated stack in the crystal of [Pt(bipy)-(en)][PF$_6$]$_2$·phe (**3**).

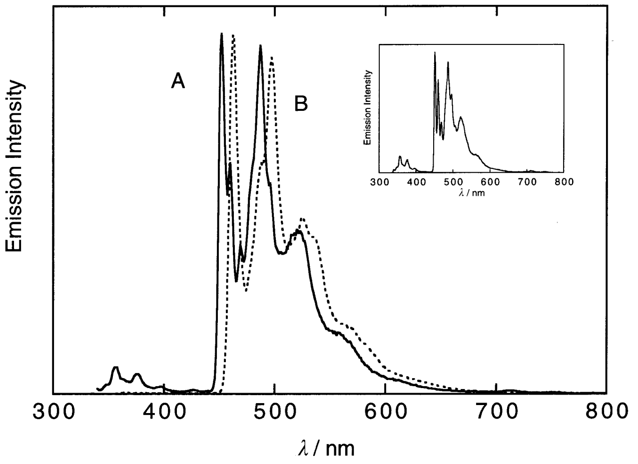

Fig. 7 Emission spectra of [Pt(bipy)(en)][PF$_6$]$_2$·phen·2H$_2$O (**1**) at 77 K: (A) EtOH–MeOH (4:1 v/v) glass, (B) neat crystal, λ_{ex} = 285 nm. Inset: emission spectrum of phen in EtOH–MeOH (4:1 v/v) at 77 K.

(Fig. 7(A)): the weak spectrum observed in the range 340–410 nm is assigned to emission from the $^1\pi\pi^*$ state of free phen because fluorescence has never been observed for [Pt(bipy)-(en)][PF$_6$]$_2$ as is usual for complexes containing heavy metals such as platinum and ruthenium. The structured spectrum observed in the range 450–700 nm is assignable to the overlapping $^3\pi\pi^*$ emission of both free phen and bipy in the [Pt(bipy)(en)]$^{2+}$ complex. It is deduced from the phosphorescence/fluorescence intensity ratio (p:f) of free phen and the composite crystal: at the excitation wavelength of 285 nm, where free phen and [Pt(bipy)(en)]$^{2+}$ have almost equal absorbance, the p:f values were estimated to be 13:1 for free phen (Fig. 7, inset), 43:1 for the composite crystal. Then the contribution of free phen and [Pt(bipy)(en)]$^{2+}$ to the $^3\pi\pi^*$ emission in Fig. 7 was estimated to be about 3:7. Thus both free phen and the [Pt(bipy)(en)]$^{2+}$ complex emit luminescence independently in glassy solution. In contrast, the $^1\pi\pi^*$ emission completely disappeared and a slightly red-shifted $^3\pi\pi^*$ emission was observed in the crystal state (Fig. 7(B)) even when it was excited at the wavelength of 265 nm where free phen was mainly excited. This is remarkable in comparison with the crystal of free phen, as a monohydrate, which emits intense fluorescence because non-radiative decay *via* the $^1n\pi^*$ state of free phen is suppressed by the hydrogen bonds between phen and crystal water.[17] The results indicate that facile energy transfer occurs between [Pt(en)(bipy)]$^{2+}$ and free phen in the integrated stack. The crystal of the original complex salt, [Pt(en)(bipy)][PF$_6$]$_2$, is known to show essentially the same emission spectrum as that in dilute glassy solution although the complex ions form π stacking involving the bipy ligands.[4,18] Thus we concluded that the π–π stacking for the [Pt(en)(bipy)]$^{2+}$ complexes themselves caused little electronic interactions in the stack. In the composite crystal **1**, however, the emission spectrum appears at *ca.* 500 cm^{-1} lower energy as shown in Fig. 7, suggesting some electronic interactions in the integrated stack. The composite crystals **2** containing [Pt(en)(phen)]$^{2+}$ also show similar emission behavior (ESI Fig. S4).

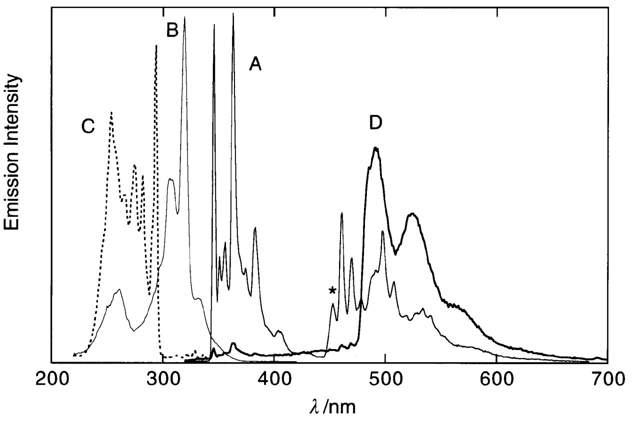

Fig. 8 Emission and excitation spectra of [Pt(bipy)(en)][PF$_6$]$_2$·phe (**3**) at 77 K: (A) emission spectrum in EtOH–MeOH (4:1v/v) at λ_{ex} = 281 nm, (B) excitation spectrum at λ_{em} = 453 nm, and (C) excitation spectrum at λ_{em} = 363 nm; (D) Emission spectrum of the neat crystal at λ_{ex} = 251 nm.

The composite crystal **3** is a good example to see the energy transfer in the integrated stack more easily because phenanthrene emits intense fluorescence ($^1\pi\pi^*$ emission) compared with phen, and the phosphorescence energy of phe is slightly different from that for the complex. Fig. 8 shows the emission and excitation spectra of **3** in EtOH–MeOH (4:1) at 77 K, as well as the emission spectrum of the neat crystal of **3**. As is the case of **1**, both fluorescence from phe (350–450 nm) and phosphorescence from phe and the [Pt(en)(bipy)]$^{2+}$ complex (450–650 nm) were observed in the glassy solution. On the basis of the spectra of the components, [Pt(en)(bipy)]$^{2+}$ and phe, the peak at 453 nm (* in Fig. 8(A)) can be assigned to the 0–0 band of the $^3\pi\pi^*$ state of the complex, while the rest of the peaks can be assigned to the $^3\pi\pi^*$ emission from phe. The excitation spectrum measured at 453 nm (Fig. 8(B)) corresponds to the absorption spectrum of [Pt(en)(bipy)]$^{2+}$ very well, whereas that monitored at 363 nm (Fig. 8(C)) corresponds to the absorption spectrum of phe. In the emission spectrum of the neat crystal (Fig. 8 (D)) the fluorescence of phe almost disappears regardless of the excitation at the strong absorption band of phe at 251 nm, and slightly red-shifted and broadened phosphorescence was observed. The phosphorescence decayed single-exponentially and the lifetime was estimated to be 19.3 μs at 78 K, which is very similar to that of the [Pt(en)(bipy)]$^{2+}$ complex (τ = 18.9 μs) but quite different from those for phe (τ = 8.4 ns for the crystal and τ > 1 ms in glassy solution at 78 K). Thus the phosphorescence of the neat crystal should be assigned to the $^3\pi\pi^*$ emission from the complex. Disappearance of both fluorescence and phosphorescence from phe clearly indicates that facile energy transfer occurs from phe to the complex. This phenomenon cannot be explained only in terms of reabsorption of the fluorescence by the complex. It is interesting that the emission state of the composite crystal **3** is the $^3\pi\pi^*$ state of [Pt(en)(bipy)]$^{2+}$ which is slightly modified in the environment of the integrated stack, whereas the $^3\pi\pi^*$ state of the complex in glassy solution is a little higher in energy ($\nu_{0\text{-}0}$ 22.1 × 10^3 cm^{-1}) than that of phe ($\nu_{0\text{-}0}$ 21.7 × 10^3 cm^{-1}).

Table 2 Crystallographic data for compounds **1**–**3**

	$[Pt(en)(bipy)][PF_6]_2\cdot phen\cdot 2H_2O$ (**1**)	$[Pt(en)(phen)][PF_6]_2\cdot phen\cdot 2H_2O$ (**2**)	$[Pt(en)(bipy)][PF_6])_2\cdot phe$ (**3**)
Formula	$C_{24}H_{28}F_{12}N_6O_2P_2Pt$	$C_{26}H_{28}F_{12}N_6O_2P_2Pt$	$C_{26}H_{26}F_{12}P_2Pt$
M	917.54	941.56	879.54
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$ (no.2)	$P2_1/c$ (no.14)	$P\bar{1}$ (no.2)
a/Å	10.837(6)	6.945(5)	11.762 (4)
b/Å	21.00(1)	35.895(8)	19.455(8)
c/Å	7.149(6)	13.249(5)	6.903(3)
α/°	91.38(6)		97.21(4)
β/°	104.02(5)	102.64(4)	105.97(3)
γ/°	87.67(4)		86.52(3)
V/Å^3	1577(1)	3223(2)	1505(1)
Z	2	4	2
μ(Mo-Kα)/mm^{-1}	4.64	4.54	4.85
Reflections measured	5900	7974	7462
Independent reflections	5572	7384	6885
R_{int}	0.043	0.074	0.057
No. of variables	424	442	406
$R1$ ($I > 2\sigma(I)$)	0.045	0.046	0.062
$wR2$ (all data)	0.102	0.152	0.227

In conclusion, the selective formation of the integrated stack of $[Pt(L)(en)]^{2+}$ (L = bipy or phen) with free phen or phe and the facile energy transfer in the stack have been elucidated.

Experimental

General

^{1}H NMR spectra were measured on Varian GEMINI 2000 and JEOL Lambda 400 spectrometers, IR spectra as KBr disks on a JASCO FT/IR8900μ and UV-VIS spectra using a Shimadzu UV-2500PC spectrometer and emission spectra on a Shimadzu RF-5300PC spectrofluorophotometer equipped with a liquid N_2 Dewar. Emission lifetimes were obtained using a Hamamatsu C4780 fluorescence lifetime measurement system, where the temperature was controlled with a Oxford DN1704 cryostat. Ligands and other chemicals were purchased and used without further purification.

Preparations of the composite crystals

The $[Pt(en)(L)][PF_6]_2$ (L = bipy or phen) complexes were prepared according to the literature procedure.[4,19] δ_H(dmso-d$_6$) for $[Pt(bipy)(en)][PF_6]_2$ 2.67 (4H, s, CH_2), 6.72 (4H, s, NH_2), 7.93 (2H, t, bipy), 8.53 (2H, t, bipy) and 8.72 (4H, d, bipy); for $[Pt(en)(phen)][PF_6]_2$ 2.76 (4H, s, CH_2), 6.94 (4H, s, NH_2), 8.28 (2H, dd, phen), 8.38 (2H, s, phen), 9.15 (2H, d, phen) and 9.17 (2H, d, phen).

Slow evaporation of an aqueous solution of $[Pt(en)(L)][PF_6]_2$ in the presence of an equimolar amount of free phen gave pale yellow crystals of $[Pt(en)(L)][PF_6]_2\cdot phen\cdot 2H_2O$ (L = bipy (**1**) or phen (**2**)). For **1**, $\tilde{\nu}_{max}$/cm^{-1} (KBr) 1509, 1477, 1453, 1424, 1323, 1251, 1176, 1139, 1055, 841br, 770, 734, 721 and 562; δ_H(dmso-d$_6$) 2.68 (4H, s, CH_2), 6.74 (4H, s, NH_2), 7.78 (2H, q, phen), 7.94 (2H, t, bipy), 8.00 (2H, s, phen), 8.50 (2H, dd, phen), 8.54 (2H, t, bipy), 8.72 (4H, d, bipy) and 9.11 (2H, dd, phen). For **2**, $\tilde{\nu}_{max}$/cm^{-1} (KBr) 1507, 1457, 1432, 1422, 1142, 1049, 838br, 733, 713 and 559; δ_H(dmso-d$_6$) 2.76 (4H, s, CH_2), 6.95 (4H, s, NH_2), 7.78 (2H, q, phen^f), 8.00 (2H, s, phen^f), 8.28 (2H, dd, phen^c), 8.37 (2H, s, phen^c), 8.50 (2H, dd, phen^f), 9.11 (2H, dd, phen^f), 9.15 (2H, s, phen^c) and 9.18 (2H, s, phen^c), where phen^f and phen^c denote free phen and coordinated phen, respectively.

The composite crystals including phenanthrene (phe), $[Pt(en)(L)][PF_6]_2\cdot phe$ (L = bipy (**3**) or phen (**4**)), were similarly obtained by slow evaporation of a methanol solution of the components. For **3**, $\tilde{\nu}_{max}$/cm^{-1} (KBr) 1501, 1477, 1455, 1323, 1304, 1245, 1166, 1056, 880br, 733, 720 and 566; δ_H(dmso-d$_6$) 2.68 (4H, s, CH_2), 6.73 (4H, s, NH_2), 7.68 (4H, m, phe), 7.85 (2H, s, phe), 7.94 (2H, t, bipy), 8.00 (2H, d, phe), 8.54 (2H, t, bipy), 8.72 (4H, d, bipy) and 8.84 (2H, d, phe). For **4**, $\tilde{\nu}_{max}$/cm^{-1} (KBr) 1525, 1456, 1437, 1310, 1243, 1175, 1056, 841br, 747, 710 and 557; δ_H(dmso-d$_6$) 2.76 (4H, s, CH_2), 6.94 (4H, s, NH_2), 7.68 (4H, m, phe), 7.85 (2H, s, phe), 7.99 (2H, d, phe), 8.28 (2H, dd, phen), 8.37 (2H, s, phen), 8.83 (2H, d, phe), 9.16 (2H, s, phen) and 9.18 (2H, s, phen).

Crystallography

Diffraction data were collected on a Rigaku AFC-7R diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Pertinent crystallographic data at 293 K are summarized in Table 2. The structures were solved by direct[20] or Patterson methods[21] and expanded using Fourier techniques.[22] The structures were refined with anisotropic thermal parameters for the non-H atoms.[23] All hydrogen atoms including those of water molecules were included for complexes **1** and **3**, while for **2** only one hydrogen atom (H25) fixed by the hydrogen bond was found among four hydrogen atoms of water molecules. An analytical absorption correction was applied. All calculations were carried out using the TEXSAN crystallographic software package.[24]

CCDC reference number 186/2320.

See http://www.rsc.org/suppdata/dt/b0/b007292n/ for crystallographic files in .cif format.

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