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Antenna behavior of donor–acceptor dye-loaded novel supramolecular framework hosts

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New guest dye cations within the channel cavities of supramolecular hosts are studied. The guest organic dyes are intercalated in the supramolecular hosts by a coprecipitation reaction to give new dye-sensitizer coordination polymers. The absorption spectra for the dye molecules within the supramolecular hosts show intense bands in the region from 500 to 700 nm due to the presence of the dyes within the parallel channels in the monomeric forms. The properties of the resulting colored polymers were investigated by IR, UV–vis, fluorescence spectra and X-ray powder diffraction, indicating the excitation energy transfer from neutral red or pyronine as donors to methylene blue or thionine as acceptors within a supramolecular system filled with a mixture of both dyes. The wide-ranging tenability of these highly organized materials offers fascinating new possibilities for exploring excitation energy transfer phenomena, and challenges for developing new photonic devices. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: supramolecular chemistry; fluorescence; dyes; energy transfer; artificial antenna; zeolite

INTRODUCTION

Various scientific applications in different areas have been found since three-dimensional (3-D) coordination polymeric compounds were discovered.[1–5] The coordination polymer of the formula $[(R_3Sn)_4Fe^{II}(CN)_6]_n$, where R = Me (**1**), Bu (**2**) or Ph (**3**), is produced by the reaction of the appropriate organotin chloride R_3SnCl with potassium ferrocyanide $[K_4Fe^{II}(CN)_6]$:[6,7]

$$4nR_3SnCl + nK_4[Fe^{II}(CN)_6] \longrightarrow [(R_3Sn)_4Fe^{II}(CN)_6]_n + 4nKCl$$

These coordination polymers exhibit a zeolite-like structure because they possess a large variety of well-defined internal structures, such as uniform cavities or channels (Fig. 1).[8] The availability of notably large cavities within the iron(II) polymers can be demonstrated chemically by the facile encapsulation of voluminous organometallic guest cations into the negatively charged host lattice $[(R_3Sn)_4Fe(CN)_6^-]_n$. Thus, numerous, mainly organic or organometallic, guest cations may be introduced quantitatively into suitable cavities of a negatively charged host network by releasing, at most, one Me_3Sn ion, leading to host–guest systems with unusual properties.[9–14]

Dye molecules are capable of absorbing light in the visible region of the electromagnetic spectrum and subsequently inducing electron transfer reactions. These dyes are either organometallic complexes or organic dye compounds, such as methylene blue (MB), thionine (TH), pyronine (PY), and neutral red (NR) (Fig. 2).[15]

Calzaferri and co-workers[16,17] studied dye molecules in zeolites as artificial antennae. The channel structure of the zeolite can be filled with appropriate dye molecules so that the packing is dense enough to fulfill the needs of fast Förster energy transfer but that each molecule still acts as a monomer.[18–21] The necessary condition of the arrangement is that energy transfer from an excited molecule to an unexcited neighbor is much faster than any other process.[16,22] The two processes of light collection and its conversion to chemical/electrochemical energy are separated from each other in natural photosynthesis. The light is absorbed by an antenna consisting of 300 to 1000 chlorophyll molecules arranged as monomers in a protein environment. This allows very fast energy transfer from an electrochemically excited

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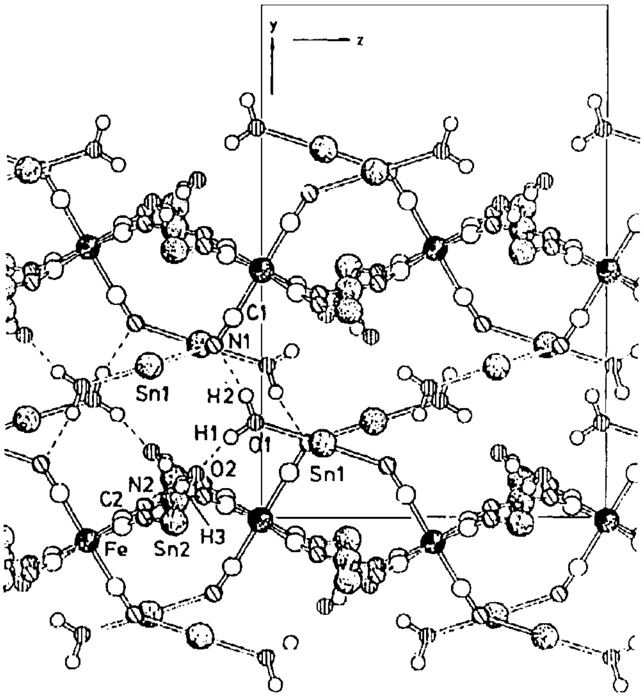
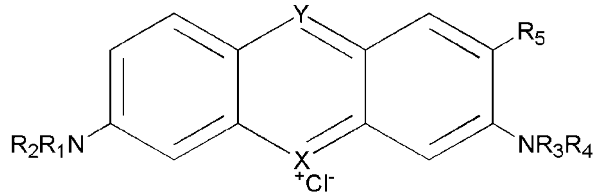


Figure 1. The structure of [$(Me_3Sn)_4Fe(CN)_6 \cdot 4H_2O$].



PY: X = O, Y = CH, $R_1 = R_2 = R_3 = R_4 = CH_3$, $R_5 = H$

NR: X = Y = N, $R_1 = R_2 = H$, $R_3 = R_4 = R_5 = CH_3$

MB: X = S, Y = N, $R_1 = R_2 = R_3 = R_4 = CH_3$, $R_5 = H$

TH: X = S, Y = N, $R_1 = R_2 = R_3 = R_4 = R_5 = H$

Figure 2. Schematic structure of donor and acceptor dyes.

molecule to its unexcited neighbor, the time scale being in the order of 1 ps.[23]

In this study, new dye-containing polymers were prepared by the coprecipitation reaction according to the following equation:

$$4nR_3SnCl + nK_4[Fe^{II}(CN)_6] + n\text{dye}^+ \longrightarrow [(\text{dye}^+)_x \times (R_3Sn)_{4-x}Fe^{II}(CN)_6 \cdot 2H_2O]_n + 4nKCl + xnR_3Sn^+$$

where $\text{dye}^+ = MB^+$, TH^+, PY^+, or NR^+. The main goal of the host–guest dye-sensitized coordination polymer is to provide the desired geometrical properties for arranging and stabilizing the encapsulated dye species. The attractive characteristics of this class of polymers suggest that these cavities may be used as an environment for providing fascinating possibilities for building an artificial antenna device.

RESULTS AND DISCUSSION

Analytical data

The elemental analysis data indicate that the dye guest compounds encapsulated within the host coordination polymers to give host–guest 3-D coordination polymers. The results show that the guest molecules encapsulated within the channels of the hosts are less than 1 mol ($x < 1$) per mole of hosts (e.g. see Table 1).

IR spectra

The 3-D coordination polymer has octahedral $Fe(CN)_6$ units that are continuously interlinked by practically planar R_3Sn fragments, with all the main-group metal atoms occupying axial trigonal-bipyramidal positions. The unit cells of these compounds may offer a better insight into construction of the lattice along the most dominant, parallel channels and perpendicular to them. The free-opening channel diameters for these supramolecular hosts are about 9.5 Å. This has to be compared with the slightly smaller opening channel diameter in the zeolite-like structure. The free space of the supramolecular hosts and the lattice parameter indicate the ability of the channels of the supramolecular hosts **1**, **2** or **3** to encapsulate cationic organic dye molecules. The monomer units of the guest dye molecules (MB, TH, Py, and/or NR) are disposed in a parallel manner, and the geometry of the

Table 1. Elemental analysis data and composition of host and host–guest 3-D coordination polymer **3**

		Anal. Found (requires) (%)				
Compound	Composition	C	H	N	Fe	Sn
3	$[(Ph_3Sn)_4Fe^{II}(CN)_6 \cdot 2H_2O]_n$	45.35 (45.72)	3.85 (4.06)	5.24 (5.33)	3.46 (3.54)	30.02 (30.15)
$[(MB)-$**3**$]_n$	$[(MB^+)_{0.8}(Ph_3Sn)_{3.2}Fe^{II}(CN)_6 \cdot 2H_2O]_n$	57.21 (57.51)	4.02 (4.16)	7.12 (7.37)	3.16 (3.50)	23.49 (23.82)
$[(PY)-$**3**$]_n$	$[(PY^+)_{0.8}(Ph_3Sn)_{3.2}Fe^{II}(CN)_6 \cdot 2H_2O]_n$	58.43 (58.61)	3.91 (4.25)	6.25 (6.73)	3.34 (3.53)	23.87 (24.03)
$[(TH)-$**3**$]_n$	$[(TH^+)_{0.9}(Ph_3Sn)_{3.1}Fe^{II}(CN)_6 \cdot 2H_2O]_n$	56.42 (56.67)	3.62 (3.87)	7.73 (7.92)	3.78 (3.82)	23.88 (23.94)
$[(PY)(TH)-$**3**$]_n$	$[(PY^+)_{0.9}(TH^+)_{0.9}(Ph_3Sn)_{2.2}Fe^{II}(CN)_6 \cdot 2H_2O]_n$	58.74 (58.82)	4.12 (4.31)	9.86 (10.04)	3.62 (3.81)	17.52 (17.85)

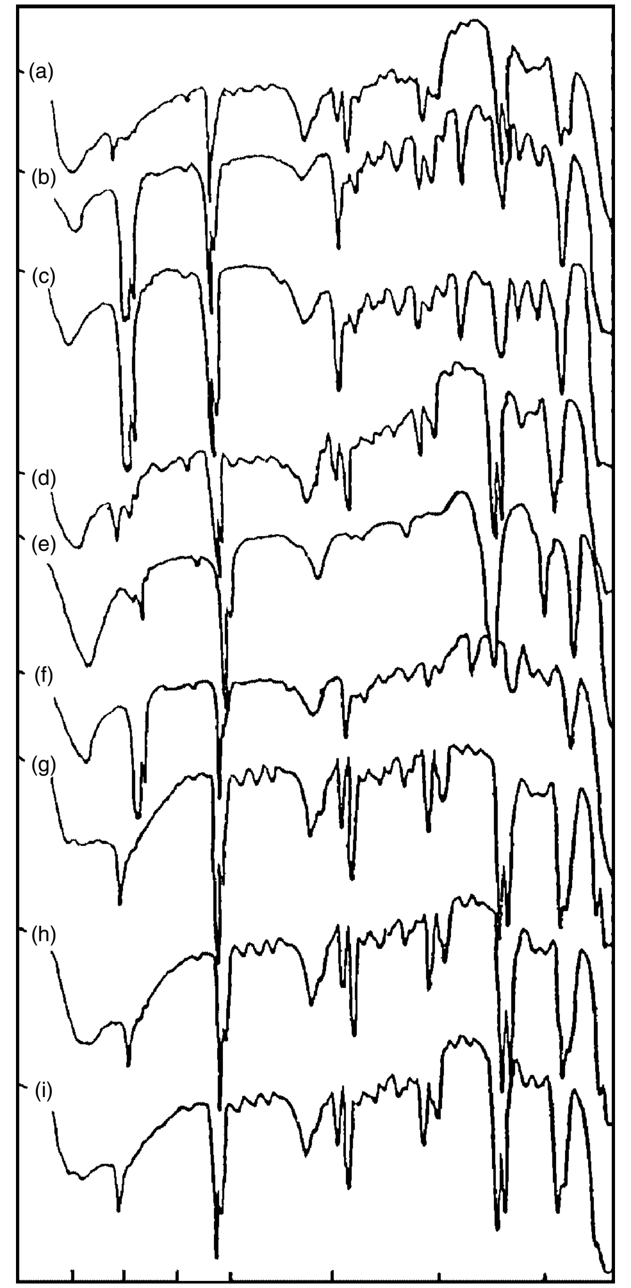


Figure 3. IR spectra for supramolecular host–guest systems: (a) $[(NR)-\mathbf{1}]_n$; (b) $[(MB)-\mathbf{1}]_n$; (c) $[(NR)(MB)-\mathbf{1}]_n$; (d) $[(PY)-\mathbf{2}]_n$; (e) $[(MB)-\mathbf{2}]_n$; (f) $[(PY)(MB)-\mathbf{2}]_n$; (g) $[(NR)-\mathbf{3}]_n$; (h) $[(TH)-\mathbf{3}]_n$; (i) $[(NR)(TH)-\mathbf{3}]_n$.

host channels prevents the formation of dimers or aggregates of dye molecules inside the host framework.

This is supported by the IR spectra of the host–guest supramolecular systems (Fig. 3). The IR spectra bands around 420 cm^{-1} and 1530 cm^{-1} were attributed to the ν(Sn–N) bonds and the vibrations of the phenyl ring respectively. The host–guest dye-sensitized coordination polymers show other characteristic bands for the guest cations between 2912 and 2921 cm^{-1} corresponding to ν(CH) (aromatic) of the phenyl ring. Also, medium to weak bands appeared at 1635–1654 cm^{-1} and 1448–1488 cm^{-1}, corresponding to ν(C=C) and ν(C=N) of the dye rings respectively. When the guest dye-cations are introduced into suitable cavities of a negatively charged host polymer, a novel supramolecular host–guest system is formed. The IR spectra display strong bands below 2100 cm^{-1}, which correspond to the stretching vibrations of the $[-Fe^{II}(CN)_6]^{4-}$ building blocks, and there are medium bands at 440–446 cm^{-1} due to the stretching vibrations of the Fe^{II}–C bond. Also, the IR spectra display medium bands at 588–596 cm^{-1} that correspond to the vibrations of the ν(Sn–C) bonds, indicating that these groups still play the role of linking $[-Fe(CN)_6]^{4-}$ building blocks and acting as connecting units to form host networks.

Electronic absorption spectra

UV–vis absorption spectra for the dye-sensitized coordination polymers were measured in Nujol mulls at room temperature (e.g. see Fig. 4).

Both the dye-sensitized coordination polymers **1, 2, 3**, and the MB, PY, TH, NR salts were measured, and the results are listed in Table 2. These spectra indicate that MB, TH, PY, and NR are present within the channels of the host supramolecular frameworks in the monomeric form. The absorption spectra of the host supramolecular frameworks display bands at 207–223 nm due to the transition from iron to cyanide as ligand (M → L transition), whereas the bands at 261 and 305 nm are due to the transition from the filled bonding orbital to the hole in the shell of the metal ions (L → M). The other band at 320 nm is due to d–d transition of the $[-Fe^{II}(CN)_6]^{4-}$ building blocks.

X-ray powder diffraction

X-ray powder diffraction for the host–guest dye-sensitized coordination polymers were studied at room temperature. The experimental powder X-ray diffraction of the host–guest supramolecular polymers are compared with the simulated X-ray diffraction, the latter being based on data resulting from the structure analysis of single crystals of **1**, **2**, and **3**. The X-ray powder diagrams for the host–guest supramolecular polymers **1**, **2**, and **3** are the same as those obtained for the host supramolecular polymers. The crystalline phase was observed to be in keeping with the probable polymeric nature of the materials. The common features of these compounds are the presence of guest-free cyanide-bridged 3-D neutral networks. These are composed of nearly planar R_3Sn units linked together with slightly distorted octahedral $Fe(CN)_6$ building blocks through the cyanide-nitrogen atoms, forming three infinite nonlinear (zigzag) chains. The channels or cavities are packed with alkyl or aryl groups bonded to tin atoms. The alky or

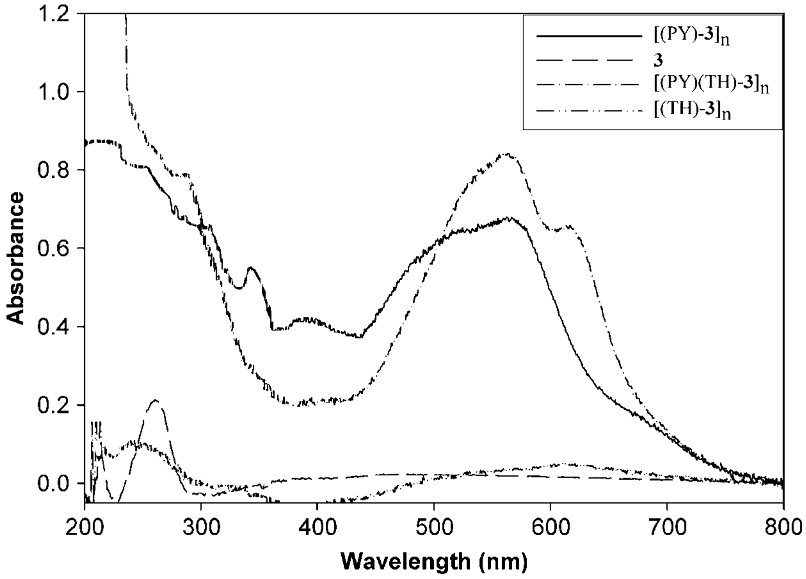


Figure 4. The electronic absorption spectra (Nujol mull) of [(PY)–**3**]$_n$, [(PY)(TH)–**3**]$_n$, [(TH)–**3**]$_n$ and **3**.

Table 2. The electronic absorption spectral data (λ_{max}) for the supramolecular host frameworks and host–guest systems

Compound	M → L (nm)	(L → M) CT (nm)	d–d (nm)	λ_{max} of cationic dyes (nm)
1[a]	219	261, 300	320	—
2[a]	—	260, 300	320	—
3[a]	220	260, 300	320	—
[(PY)–**1**]$_n$	215	268, 301	355	552
[(PY)(MB)–**1**]$_n$	210	272, 305	354	514, 562, 610, 665
[(PY)(TH)–**1**]$_n$	212	271, 305	359	512, 565, 639
[(PY)–**2**]$_n$	223	270, 300	355	555
[(PY)(MB)–**2**]$_n$	218	259, 303	351	517, 664
[(PY)(TH)–**2**]$_n$	216	267, 303	353	515, 642
[(PY)–**3**]$_n$	221	269, 300	356	560
[(PY)(MB)–**3**]$_n$	219	271, 303	355	570, 658, 715
[(PY)(TH)–**3**]$_n$	217	269, 304	354	518, 641
[(NR)–**1**]$_n$	214	274, 301	350	561
[(NR)(MB)–**1**]$_n$	209	269, 300	352	519, 662
[(NR)(TH)–**1**]$_n$	207	266, 302	355	515, 571, 642
[(NR)–**2**]$_n$	218	268, 304	351	565
[(NR)(MB)–**2**]$_n$	213	270, 305	356	522, 665
[(NR)(TH)–**2**]$_n$	214	267, 302	357	574, 646
[(NR)–**3**]$_n$	223	269, 300	350	558
[(NR)(MB)–**3**]$_n$	220	271, 304	357	520, 532, 641
[(NR)(TH)–**3**]$_n$	217	268, 303	358	568, 642

[a] Data were taken from Ref. 5.

aryl groups are distorted over three positions, with their trigonal arrangements preserved. The arrangement of the channels is significantly different from those in similar coordination polymers. The difference between the structures of methyl-, butyl-, and phenyl-tin compounds arises from the constraints imposed by Fe–CN–Sn bonds. The change in the R group results in a higher point-group symmetry for the iron atom. The diameters of the free opening channels or cavities for the hosts (**1**–**3**) are ~8.8–9.5 Å; this allows encapsulation of dye compounds and formation of novel guest–host 3-D coordination polymers. The intensities of the X-ray lines for the host–guest supramolecular systems are less than the intensities of the host supramolecular polymers. This is due to the formation of new structures which exhibit a less crystalline phase. The main peaks observed in the X-ray powder diffraction patterns are shown in Fig. 5.

Electronic emission spectra

Emission spectra were recorded at room temperature. The fluorescence emission spectra of the dye within the host supramolecular frameworks under study are different according to the type of dye. The MB or TH within host supramolecular systems exhibit very weak intense emission bands, whereas the host–guest supramolecular systems containing PY or NR show intense emission bands. Fluorescence quenching can take place via long-range dipole–dipole energy migration from the donor (D) to the acceptor (A). In this case, the energy migration processes occur when the separation distance between the D and A species is at least 20 Å and the molecules are in an attic systems. According to this hypothesis, the absorption spectra of the dyes within the host supramolecular frameworks are well enough separated so that it is possible to excite only one

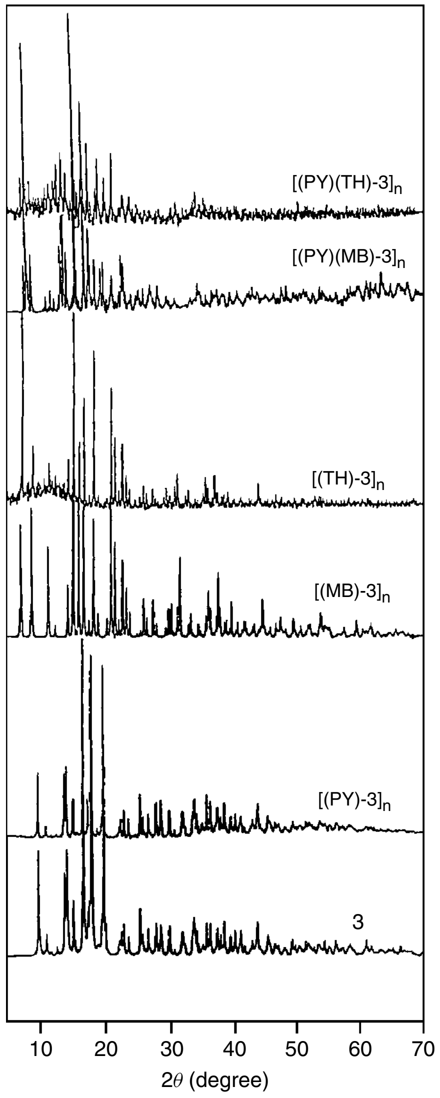


Figure 5. The experimental X-ray diffractogram of the host (**3**) and its host–guest systems.

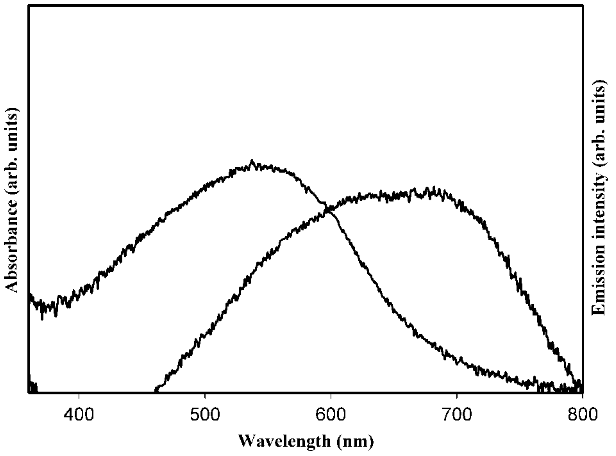


Figure 6. The spectral overlap of the MB as acceptor and NR as the donor. The emission spectrum of [(NR)–**2**]$_n$ (right) and absorption spectrum of [(MB)–**2**]$_n$ (left), measured as Nujol mulls.

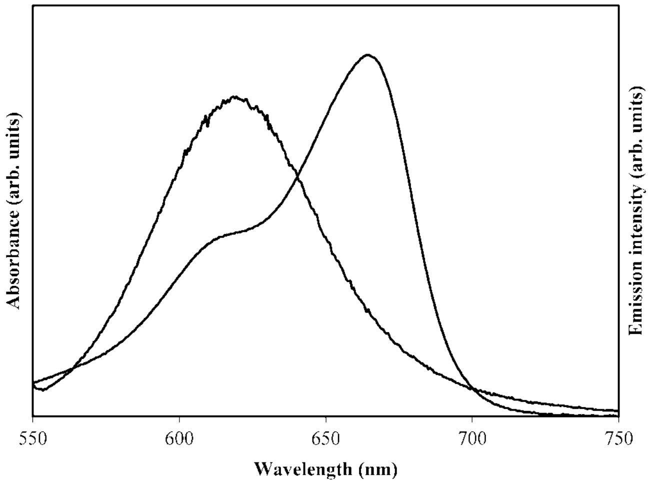


Figure 7. The spectral overlap of the MB as acceptor and NR as the donor. The emission (right) and absorption (left) spectra of NR and MB in H_2O.

of them in a mixture of both dyes. The emission spectra for host–guest supramolecular systems were measured at two different excitation wavelengths, i.e. 470 nm and 490 nm, where the absorption of MB and TH can be neglected compared with those containing PY and NR. The energy migration between the dyes is more efficient in the presence of the novel host supramolecular frameworks **1**, **2**, and **3** due to the increased spectral overlaps between the absorption of MB or TH and the emission of PY and NR (Figs 6 and 7).

The emission spectra of the MB or TH within the host supramolecular frameworks are established over that of the originally excited PY or NR molecules within the host frameworks (Fig. 8). This means that the dye molecules are arranged as monomers within the host frameworks. This allows a fast energy migration from PY or NR to MB or TH within the channels of the host matrix (Fig. 9).

The mechanistic pathway explaining this rapid energy migration is shown in Scheme 1. According to this mechanism, we observed that if the excited donor reaches acceptor molecules, the energy transfer becomes very probable and hence quenching occurs. However, if the internal conversion is very fast compared with the quenching process, fluorescence emission from A can be observed.

In conclusion, the geometrical constraints of the supramolecular hosts allow the cationic dye molecules to be encapsulated within the parallel channels to form novel

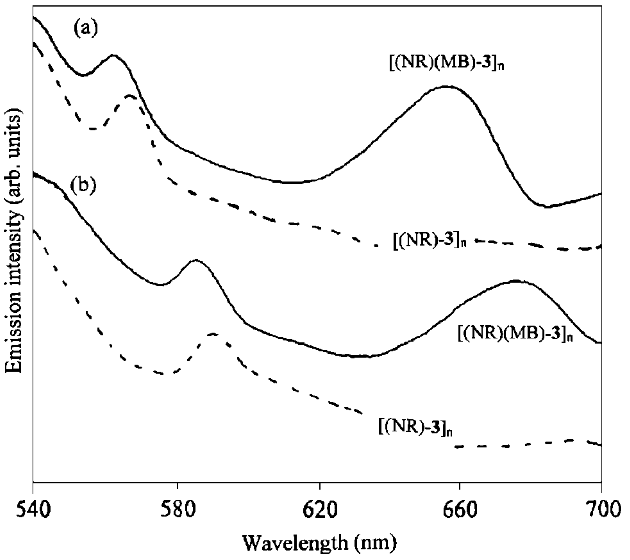


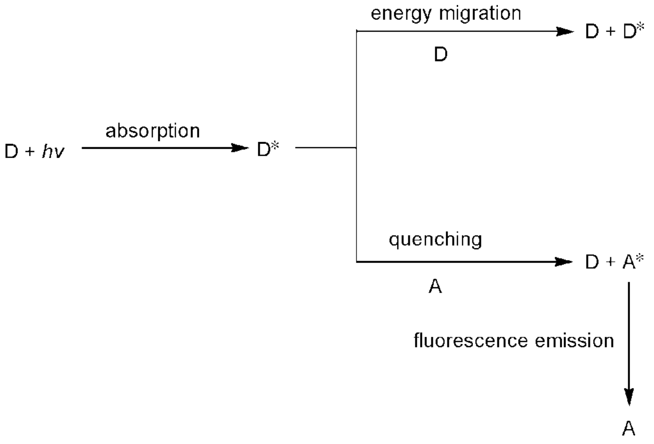
Figure 8. Emission spectra of a powder $[(NR)-\mathbf{3}]_n$ and $[(NR)(MB)-\mathbf{3}]_n$ at excitation wavelengths (a) 470 nm and (b) 490 nm. Both spectra have been measured with the same sensitivity.

host–guest systems. Different measurements of the encapsulated dyes indicate that the dye molecules are arranged as monomers within the host frameworks. The encapsulation of donor–acceptor dyes within host supramolecular framework systems can be used to build artificial antennae. An excitation energy transfer from PY or NR as a donor to MB or TH as an acceptor occurs within the channels of supramolecular systems filled with a mixture of both dyes.

EXPERIMENTAL

Materials and methods

The reagents and all chemicals were used as obtained without further purification. All dyes were encapsulated within the channels of the coordinated host polymers by the coprecipitation method. A mixture of R_3SnCl and $K_4[Fe(CN)_6]$, in 3:1 ratio, and a molar ratio of dyes was stirred in a 1:2 water/acetone mixture at room temperature for 24 h. The precipitate was filtered off, and the resulting colored supramolecular host–guest system was washed sequentially with water and/or acetone and dried under vacuum at room temperature.



Scheme 1. Mechanistic pathway for rapid energy migration: D = PY or NR; A = MB or TH.

Instruments

Elemental analyses were performed using a Perkin–Elmer 2400 automatic elemental analyzer. UV–vis spectra were recorded on a Shimadzu 3101 PC spectrophotometer using Nujol mulls. IR spectra were determined using KBr discs on a Perkin–Elmer SP 1430 IR spectrophotometer. The X-ray diffractograms were measured using a Debye–Scherrer PW 1050 ($Cu_x K\alpha$; nickel filter) instrument (Philips). Emission spectra were obtained using a Perkin–Elmer LS 50B luminescence spectrometer.

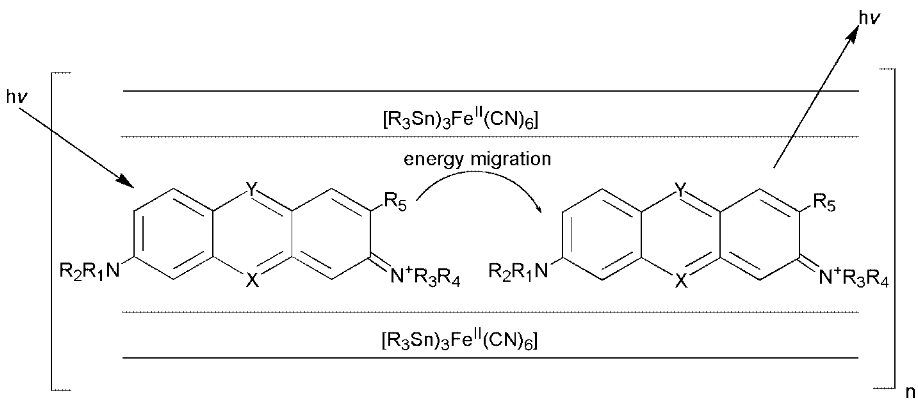


Figure 9. Schematic view of the donor–acceptor energy transfer within the host polymer channel.

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