Organic core/diffuse-shell nanorods: fabrication, characterization and energy transfer†

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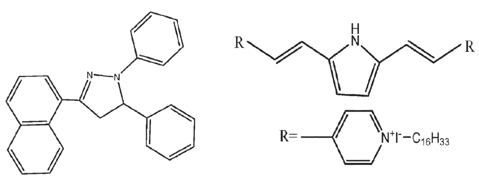
We successfully prepared organic core/diffuse-shell nanorods, which presents fluorescence resonance energy transfer from the core to shell components.

In recent years, there have been considerable interests in composite nanostructures due to their possibility for combining multi-functional properties from different components. One extremely attractive example is core/shell nanostructures. Up to now, many different types of core/shell nanostructures have been fabricated, including inorganic/inorganic,[1,2] inorganic/organic,[3] inorganic/polymer,[4] organic/polymer[5] and polymer/polymer types.[6] However, there are fewer reports on core/shell nanostructures made from organic small molecules (OSMs) as compared with those of inorganics, especially core/shell nanostructures between OSM and OSM. The electronic and optical properties of OSM crystals are primarily different from those of inorganic metals and semiconductors because of the presence of van der Waals intermolecular interactions.[7] It has been demonstrated that fluorescence resonance energy transfer (FRET) based on the doping technique provides an effective way to improve the luminescence efficiency and to tune the emission color of electroluminescent materials.[8] FRET occurs *via* the dipole–dipole coulombic resonance interaction between the donor and acceptor through space, thus is long-range in character and does not require the physical contact of the interacting partners.[9] This inspired us to fabricate organic core/shell nanostructures and to study the FRET between the core and shell components.

In this work, 1,5-diphenyl-3-(naphthalene-4-yl)-1*H*-pyrazoline ($C_{25}H_{20}N_2$, DPNP) and 2,5-bis(2-(*N*-hexadecylpyridinium-4-yl)-vinyl)pyrrole iodide ($C_{50}H_{81}I_2N_3$, Dye 1) were synthesized (see Scheme 1 and ESI†) as model compounds. The nanorods of DPNP were prepared by employing the reprecipitation method.[10,11] In a typical preparation, 100 μL of DPNP solution in acetonitrile (10^{-3} M) was rapidly injected into 4 mL ultrapure water with stirring, and aged about 2 h for the formation of the pristine nanorods. Then 100 μL of Dye 1 solution in ethanol (5×10^{-4} M) was quickly added into the above nanodispersed system under stirring, and aged for another 3 h. Finally, the nanodispersed system was filtered on the surface of an alumina membrane with an average porous size of 100 nm (Whatman International Ltd.), and washed several times using ultrapure water in order to remove residual Dye 1.



Scheme 1 Structures of model compounds of DPNP (left) and Dye 1 (right).

A scanning electron microscopy (SEM) image (Fig. 1(A)) shows that the pristine nanorods of DPNP have an average width of 200 nm and a length of several microns. The formation of DPNP nanorods may benefit from both the molecular structure of DPNP

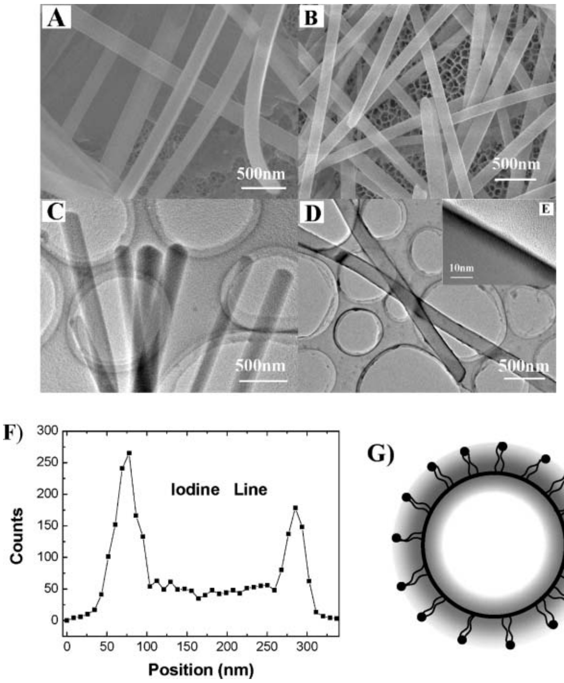


Fig. 1 (A) SEM and (C) TEM images of the pristine nanorods of DPNP; (B) SEM and (D) low-magnification TEM and (E) high-magnification TEM images of DPNP/Dye 1 core/diffuse-shell nanorods; (F) HRTEM-assisted EDS line of elemental iodine analysis across the section of a single core/diffuse-shell nanorod. (G) Schematic illustration of the section of the core/diffuse-shell nanorod. Scale bars: (A–D) 500 nm; (E) 10 nm.

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(containing electron donor and acceptor at 1- and 3-positions) that may induce π–π stacking as well as the kinetic growth of a one-dimensional nanostructure.[12,13,‡] The SEM image of the sample modified by Dye 1 (Fig. 1(B)) also shows uniform rod-like shapes with an average width of 200 nm, similar to the pristine nanorods. However, significant differences are observed between the pristine and Dye 1-modified nanorods by means of transmission electron microscopy (TEM). A TEM image of the pristine nanorods of DPNP (Fig. 1(C)) is consistent with the observation by SEM, while a TEM image of the sample modified by Dye 1 (Fig. 1(D)) reveals clearly a core/shell structure. The high-magnification TEM image of Fig. 1(E) clarifies that the thickness of the shell layer is about 5–10 nm. Fig. 1(F) shows the high-resolution TEM (HRTEM) assisted energy-dispersive X-ray spectroscopy (EDS) line analysis across the section of a single core/shell nanorod (see Fig. 1(G)). Two peaks of the element iodine at both edges can be identified, and are separated by a distance of ∼200 nm, equal to the width of nanorod observed by electron microscopy. Therefore, Dye 1 molecules have been successfully coated on the surface of the pristine nanorods of DPNP. It can also be seen from Fig. 1(F) that the signal intensity of iodine between two peaks is not zero, indicating the distribution of iodine on the whole surface of the nanorod. Furthermore, Fig. 1(F) reveals that the thickness of iodine layer extends around 50 nm, larger than the value of 5–10 nm determined by TEM. Due to the solid-state diffusion, there must be a diffuse layer of iodine extending into the pristine nanorod, forming a core/diffuse-shell structure. This is not like the case that it is understood in the inorganic community, where the interface between the core and shell is atomically thin.

Fig. 2(A) depicts that the ξ-potential of Dye 1 itself in water increases with increasing the quantity (V_{Dye1}) of the stock Dye 1–ethanol solution (5×10^{-4} M) that is injected into 4 mL water, however, it reaches a constant value of +63 mV when $V_{\mathrm{Dye\ 1}} > 100$ μL. This suggests that Dye 1 molecules form micelle-like structures in the aqueous phase with a critical micelle concentration (CMC) around 1.25×10^{-5} M.[14] The positive ξ-potential of Dye 1 in water stems from the positively charged groups of Dye 1 (Scheme 1), which are hydrophilic and outward, as the long alkyl chains (Scheme 1) would aggregate to form a hydrophobic core in water.[14] It should be pointed out that the nanodispersed system of the pristine nanorods in water shows a negative ξ-potential of −44 mV. As shown in Fig. 2(B), the negative ξ-potential of the pristine nanorods in water gradually changes to positive by adding Dye 1, and finally reaches +63 mV when $V_{\mathrm{Dye\ 1}} > 50$ μL. This suggests that the presence of DPNP nanorods provides a solid/liquid interface, which facilitates the adsorption of Dye 1 molecules as a result of the hydrophobic interactions between the alkyl chains of Dye 1 and DPNP molecules located on the surface of nanorods. The adsorption of Dye 1 molecules on the pristine nanorods results in the switch of ξ-potential from negative to positive, and is responsible for the formation of the Dye 1/DPNP core/diffuse-shell nanorods. The counter ions of Dye 1 molecules, I^-, have a ionic radius of 2.06 Å, might diffuse and extend into the pristine nanorod, forming a diffuse layer.

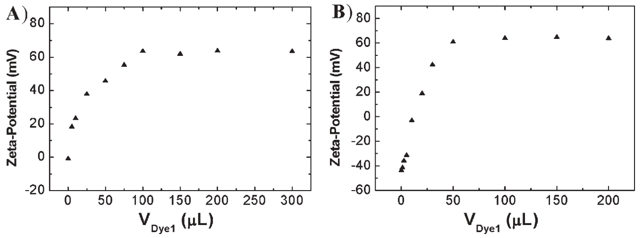

Fig. 2 The ξ-potential of Dye 1 *vs.* $V_{\mathrm{Dye\ 1}}$ of the stock Dye 1 solution in ethanol (5×10^{-4} M) injected into 4 mL water in the absence (A) and (B) presence of pristine nanorods of DPNP. See text for details.

We also characterized the formation of Dye 1/DPNP core/diffuse-shell nanorods by using spectroscopic methods. Fig. 3(A) presents the diffuse reflectance UV-vis absorption spectra of the pristine nanorods (curve 1) and the Dye 1 powder (curve 3). As compared with the absorption of DPNP monomers in dilute solution (see Fig. S2 in ESI†), the absorption band at 425 nm in spectrum 1 is ascribed to the aggregate state and is an indication of the formation of DPNP nanorods.[11,15] After 100 μL of Dye 1 solution in ethanol (5×10^{-4} M) was added into the aqueous nanodispersed system of the pristine nanorods, samples were filtered at different aging intervals. It can be seen from Fig. 3(B) that the absorbance of Dye 1 at 530 nm gradually increases as the aging time increases, while the absorbance of DPNP almost stays the same. This confirms that more and more Dye 1 molecules

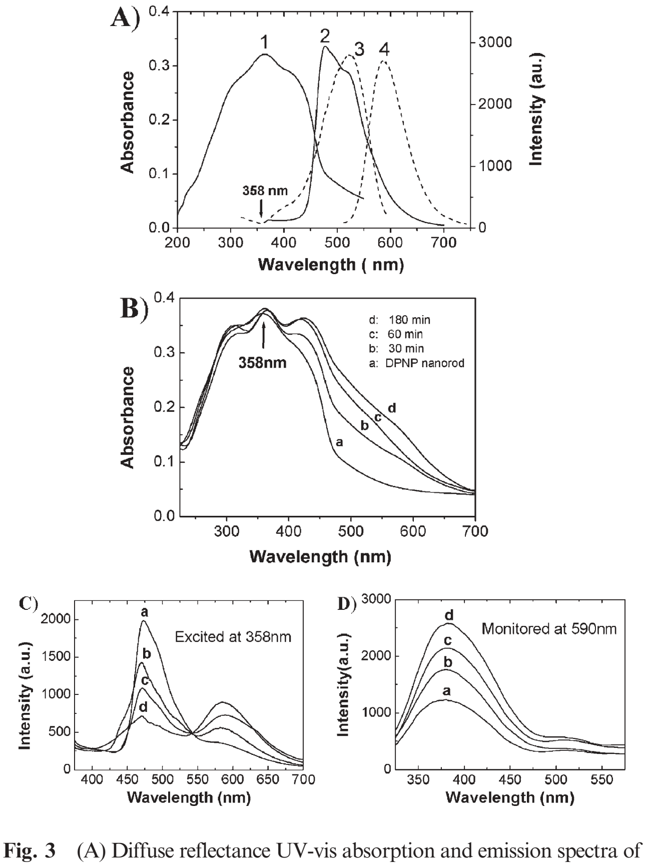

Fig. 3 (A) Diffuse reflectance UV-vis absorption and emission spectra of the pristine DPNP nanorods (solid lines 1 and 2) and Dye 1 powder (dashed lines 3 and 4). The diffuse reflectance absorption (B), the steady-state fluorescence emission (C) and excitation (D) spectra of DPNP/Dye 1 core/diffuse-shell nanorods obtained at different aging intervals. Except for curve **a** in (B) that is for the pristine DPNP nanorods, the aging times after adding Dye 1 solution into the DPNP nanodispersed system are 5, 30, 60 and 180 min, for **a**, **b**, **c** and **d**, respectively. All the samples were filtered on the surface of alumina membranes.

Table 1 The decay times of the fluorescence of DPNP at 475 nm in the pristine nanorods and the core/diffuse-shell nanorods obtained at different aging intervals. The excitation wavelength is 375 nm

	τ_1		τ_2		
Aging time/min	ns	$\%_1$	ns	$\%_2$	τ^a/ns
0	1.36	86	4.53	14	1.82
5	1.16	82	3.75	18	1.62
30	0.97	79	3.31	21	1.47
60	0.75	77	2.78	23	1.22
180	0.53	77	2.55	23	0.99

[a] Average fluorescence lifetime, $\tau = (\tau_1\%_1 + \tau_2\%_2)/100$.

adsorb on the pristine nanorods with increasing the aging time. Under conditions of the aging time >180 min, the absorbance of Dye 1 reaches a constant value since the adsorption and desorption of Dye 1 on DPNP nanorods reaches an equilibrium in water.

Fig. 3(A) shows that the diffuse reflectance UV-vis absorption spectrum of Dye 1 powder (curve 3) overlaps very well with the steady-state emission spectrum of the pristine nanorods of DPNP (curve 2) in the wavelength range of 450–600 nm. This is essential for the occurrence of FRET.[9] It is known that besides the spectral overlap, the rate of FRET also depends upon the relative orientation of the donor and acceptor transition dipoles, and the distance between these molecules.[9] The latter, *i.e.* the so-called Förster radius, is about 2–5 nm[9] at the same order of the diffuse-shell thickness. Therefore, FRET from the DPNP core to the Dye 1 shell is possible in our core/diffuse-shell nanorods. Indeed, although the absorbance of Dye 1 at 358 nm is very weak (~5% of that at 530 nm, see the arrow in Fig. 3(A)), the emission spectra of Dye 1/DPNP core/diffuse-shell nanorods excited at 358 nm (Fig. 3(C)) shows that the contribution of Dye 1 around 590 nm gradually increases with increasing the aging time, meanwhile, the contribution of DPNP around 470 nm decreases. The corresponding excitation spectra monitored at 590 nm shows that the enhanced emission of Dye 1 results from the energy levels of DPNP (Fig. 3(D)). Thus, FRET from the DPNP core to the Dye 1 shell is responsible for the enhanced emission of Dye 1 in the core/diffuse-shell nanorods.

Table 1 shows the fluorescence lifetimes for the pristine and core/diffuse-shell nanorods. The fluorescence decay of DPNP monomers in ethanol solution is monoexponential with a lifetime of 1.43 ns at 500 nm. However, the fluorescence of the pristine nanorods shows biexponential decay. The short lifetime (τ_1) of 1.36 ns is comparable to the value of the monomer, thus is ascribed to the molecular state, while the long one (τ_2) might be relative to the aggregate state of DPNP molecules in the nanorod.[15] As shown in Table 1, both τ_1 and τ_2 of the core/diffuse-shell nanorod become shorter as compared with those of the pristine nanorods. Therefore both the molecular and aggregate states of DPNP molecules in the core/diffuse-shell nanorod might be involved in the FRET process from the DPNP core to the Dye 1 shell. The average fluorescence lifetimes (τ) of the core/diffuse-shell and pristine nanorods are 0.99 and 1.82 ns at 0 and 180 min, respectively, indicating that the DPNP fluorescence is quenched by a factor of two due to the FRET process.§ However, the steady-state measurement in Fig. 3(C) discloses that the DPNP fluorescence in the core/diffuse-shell nanorods is quenched totally by a factor of four as compared with the pristine nanorods. As discussed above, the counter ions of Dye 1, I^-, form a diffuse layer extending into the pristine nanorod. Note that iodine can be an effective fluorescence quencher due to the static quenching (in this process the fluorescence decay of the unquenched fluorophore does not change).[9] Therefore, both FRET to Dye 1 and iodine quenching are occurring in DPNP/Dye 1 core/diffuse nanorods.

In conclusion, organic core/diffuse-shell nanorods have been successfully fabricated by two steps: (i) the preparation of uniform DPNP nanorods by a simple reprecipitation method; (ii) the adsorption of Dye 1 on the surface of DPNP nanorods through hydrophobic interactions. The FRET from the DPNP core to the Dye 1 shell can be adjusted by controlling the aging time. Such organic composite nanostructure with tunable FRET from the core to the shell might be promising for multifunctional nanomaterial in optoelectronic nanodevices.

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Notes and references

‡ By using the same procedure, DPNP molecules form spherical particles/cubic nanocrystals at low chemical potential,[11] rather than the nanorods in the present study at high chemical potential. This might relate to the kinetic growth of one-dimensional nanostructures of organic semiconductors, and is under investigation in this laboratory.

§ Considering the aggregate absorption of the nanorods at 425 nm, the donor–donor Förster overlap for nanorods (between spectra 1 and 2 in Fig. 3(A)) is not poor. Therefore, energy migration through the aggregate state in nanorods might be possible, and amplifies the shell quenching.

1 F. Qian, S. Gradečak, Y. Li, C. Y. Wen and C. M. Lieber, *Nano Lett.*, 2005, **5**, 2287.
2 M. Green, *Small*, 2005, **1**, 684.
3 C. W. Chan and S. Nie, *Science*, 1998, **281**, 2016.
4 J. Jang, J. Ha and B. Lim, *Chem. Commun.*, 2006, **15**, 1622.
5 H. G. Zhu and M. J. McSchane, *J. Am. Chem. Soc.*, 2005, **127**, 13448.
6 H. Y. Huang, E. E. Remsen and K. L. Wooley, *Chem. Commun.*, 1998, 1415.
7 E. A. Silinsh, *Organic Molecular Crystals: Their Electronic States*, Springer-Verlag, Berlin, 1980.
8 A. D. Peng, D. B. Xiao, Y. Ma, W. S. Yang and J. N. Yao, *Adv. Mater.*, 2005, **17**, 2070; C. W. Tang, D. J. Williams and J. C. Change, *US Pat.*, #5 294 870 1944; C. W. Tang, S. A. VanSlyke and C. H. Chem, *J. Appl. Phys.*, 1989, **65**, 3610.
9 J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Plenum Press, New York, 1999; N. J. Turro, *Modern Molecular Photochemistry*, Benjamin Cummings Publishing Co., Menlo Park, CA, 1978.
10 H. Kasai, H. S. Nalwa, H. Oikawa, S. Okda, H. Matsuda, N. Minami, A. Kakuta, K. Ono, A. Mukoh and H. Nakanishi, *Jpn. J. Appl. Phys., Part 2*, 1992, **31**, L1132.
11 H. B. Fu, X. H. Ji, X. H. Zhang, S. K. Wu and J. N. Yao, *J. Colloid Interface Sci.*, 1999, **220**, 177.
12 Z. Y. Tian, Y. Chen, W. S. Yang, J. N. Yao, L. Y. Zhu and Z. G. Shuai, *Angew. Chem., Int. Ed.*, 2004, **43**, 4060.
13 K. Balakrishnan, A. Datar, T. Naddo, J. L. Huang, R. Oitker, M. Yen, J. C. Zhao and L. Zang, *J. Am. Chem. Soc.*, 2006, **128**, 7390; P. Jonkheijm, P. V. D. Schoot, P. H. J. Schenning and E. W. Meijer, *Science*, 2006, **313**, 80.
14 J. Leja, *Surface Chemistry of Froth Flotation*, Plenum Press, New York, 1982; D. Myers, *Surfactant Science and Technology*, 2nd edn, VCH, 1992.
15 H. B. Fu and J. N. Yao, *J. Am. Chem. Soc.*, 2001, **123**, 1434.