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Noncovalent assemblies of CdSe semiconductor quantum dots and an amphiphilic long-chain *meso*-arylporphyrin

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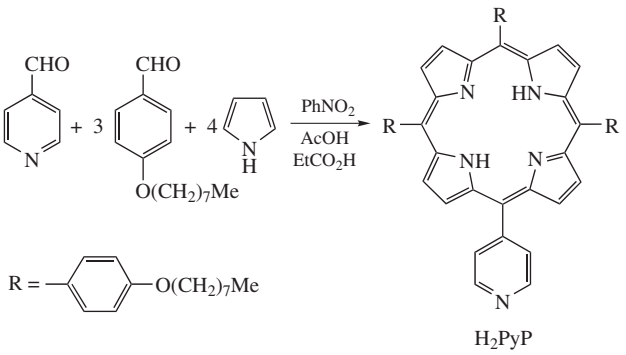
The spectroluminescent properties of the noncovalent assemblies of CdSe semiconductor quantum dots with 5-(4-pyridyl)-10,15,20-tris(4-*n*-octaoxyphenyl)porphyrin and the efficiency of energy transfer from the quantum dots to the porphyrin molecule by the Förster resonant energy transfer mechanism were evaluated.

Hybrid photoactive systems based on tetrapyrrole molecules and inorganic semiconductor nanocrystals are of considerable interest since they are promising for practical applications in technology,[1–3] biology[4] and medicine.[5,6] Macrocyclic tetrapyrrole compounds (porphyrins, phthalocyanines and porphyrazines) possess high thermal and chemical resistance together with unique photophysical properties, and they can be synthesized in required amounts. Semiconductor nanocrystals (quantum dots) are effective light energy accumulators and donors due to their photophysical properties. They are characterized by high quantum yields of luminescence (60–80%), photostability and high molar absorption coefficients (10^5–10^6 dm^3 mol^{-1} cm^{-1}). Their assemblies with porphyrins are of special interest because the Förster resonant energy transfer (FRET) can occur in these systems and this is promising for the development of light-collecting materials and sensors. Organic-inorganic assemblies of this type can be created due to both covalent[6,7] and noncovalent interactions.[1,3,8,9] It is well known that the formation of quantum dot–porphyrin assemblies is accompanied by donor (quantum dot) fluorescence quenching owing to photoinduced electron transfer[10] or energy transfer.[11] The luminescence quenching of CdSe/ZnS quantum dots by the molecules of symmetrical 5,10,15,20-tetrapyridylporphyrin was observed;[5,9] asymmetrically substituted pyridyl-containing porphyrins were not studied previously in the development of donor–acceptor systems of this kind.

The aim of this work was to obtain the photoactive complexes of CdSe quantum dots with amphiphilic 5-(4-pyridyl)-10,15,20-tris(4-*n*-octaoxyphenyl)porphyrin due to noncovalent coordination interactions and to study energy transfer from the quantum dots to porphyrin molecules in these complexes.



Scheme 1

Initially, we synthesized new amphiphilic porphyrins containing a pyridine residue and three long-chain alkyl substituents in the *meso* positions of the macrocycle. The introduction of aliphatic substituents ensures the solubility of porphyrins and their conjugates[12] in nonpolar solvents and facilitates surface immobilization and structurization (liquid-crystal properties[13] and Langmuir–Blodgett films[14]).

5-(4-Pyridyl)-10,15,20-tris(4-*n*-octaoxyphenyl)porphyrin (H_2PyP) was synthesized by monopyrrole condensation in a mixture of nitrobenzene, acetic acid and propionic acid in a ratio of 1 : 1 : 2 (Scheme 1).[15,†] The mixture of acids served as a solvent and acid catalyst, and nitrobenzene served as a mild oxidizing agent. The product was purified by column chromatography on silica gel. The product yield was 12% (See Online Supplementary Materials). The UV-VIS spectrum exhibited a Soret band at 418 nm and four absorption bands (etio-type spectrum). The porphyrin was identified by ^{1}H, ^{13}C NMR spectroscopy and mass spectrometry. The ^{1}H NMR spectrum exhibited signals due to pyridine

† Domestic calcium hydride, phosphorus pentoxide and organic solvents; 4-pyridylcarboxaldehyde, pyrrole and potassium carbonate from Sigma; and silica gel G60 from Merck were used. Dichloromethane and pyrrole were distilled from phosphorus pentoxide and calcium hydride, respectively; the alkoxy-substituted benzaldehyde was obtained according to a published method.[20] The highly monodisperse nanocrystals of CdSe coated with *n*-trioctylphosphine (TOPO) had an absorption maximum at 565–575 nm and a corresponding luminescence maximum at 585–595 nm (quantum dot diameter, 4.0 nm; $\varepsilon = 2.5\times10^5$). The quantum yield of luminescence of the quantum dots was $\Phi_{OD} = 50\%$ (Lumidot™). The absorption of the solution of quantum dots was no higher than 0.1 in order to prevent nonlinear absorption and reabsorption effects. The noncovalent quantum dot–porphyrin assemblies were prepared by the stepwise titration of 2 ml of a 3.6×10^{-7} M solution of quantum dots in toluene with 20 μl portions of a 2.2×10^{-5} M solution of porphyrin in toluene.

The fluorescence spectra were measured on a Cary Eclipse spectrofluorometer (Agilent). The ^{1}H and ^{13}C NMR spectra of the test solutions in $CDCl_3$ or $(CD_3)_2SO$ were measured on a Bruker MSL-300 pulse Fourier transform spectrometer. Tetramethylsilane or boron trifluoride etherate was used as an external standard. The high resolution MALDI-TOF spectra were obtained on an Ultraflex mass spectrometer (Bruker) using 2,5-dihydroxybenzoic acid as a matrix. The electronic spectra were recorded on a TermoSpectronic Helios Alpha spectrophotometer in quartz cuvettes with an optical path length of 1 cm.

protons (two doublets at 8.18 and 9.04 ppm with J 5.97 and 5.88 Hz, respectively) and also signals due to β-pyrrole protons (a multiplet at 8.90–8.94 and a doublet at 8.79 ppm with J 4.82 Hz) with an integrated intensity ratio of 1 : 3, which is indicative of the asymmetrical system formation.

The CdSe quantum dots with a long-wave absorption band maximum at 565–575 nm and corresponding luminescence maximums at 585–595 nm (quantum dot diameter, 4.0 nm; $\varepsilon = 2.5\times10^5$) were used for the preparation of the quantum dot – porphyrin assemblies. The overlapping of the luminescence spectra of the quantum dots and the absorption spectra of H_2PyP is a necessary condition for energy transfer from the quantum dots to the porphyrin (Figure S1, Online Supplementary Materials). The noncovalent quantum dot–porphyrin assemblies were obtained in toluene by the stepwise titration of a solution of quantum dots with a porphyrin solution until saturation. Figure 1 shows the luminescence and absorption spectra of quantum dots on the addition of H_2PyP porphyrin. The quantum dot luminescence quenching and a gradual increase in the luminescence of H_2PyP porphyrin were observed, which suggest the formation of the quantum dot – porphyrin assemblies. A gradual increase in the Soret band intensity of H_2PyP ($\lambda = 423$ nm) was observed in the absorption spectrum.

Assuming that a static model of donor fluorescence quenching[16] is true for this system, we used the Stern–Volmer equation to determine the association constant K_a of the quantum dot–H_2PyP complex:

$$I_0/I - 1 = K_a[Q]. \quad (1)$$

Figure 2(*a*) shows the experimental Stern–Volmer dependence, which is linear to indicate the presence of one quenching mechanism. On this basis, we estimated the association constant of the quantum dot–H_2PyP complex at $K_a = 1\times10^6$ dm^3 mol^{-1}.

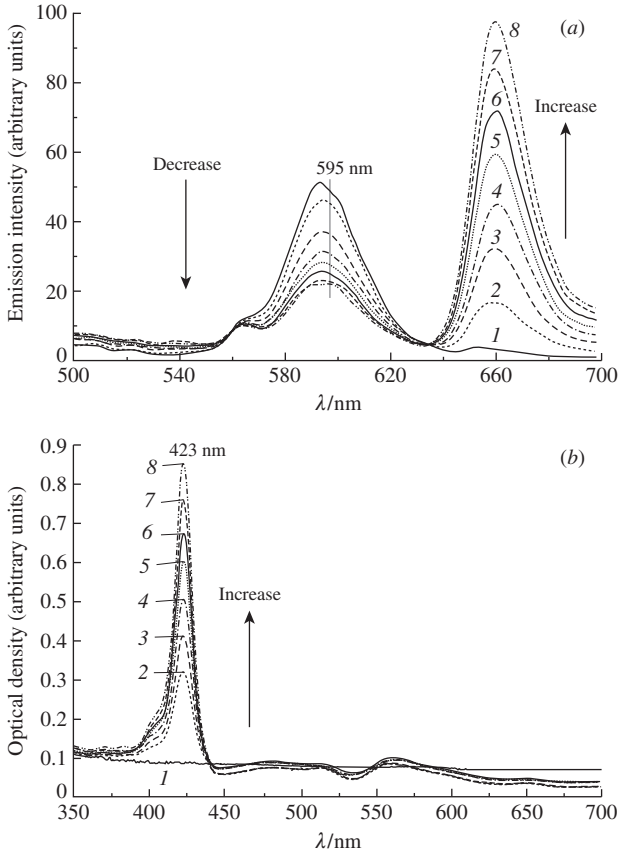


Figure 1 (*a*) Luminescence (λ_{ex} = 470 nm) and (*b*) absorption spectra of CdSe quantum dots and H_2PyP in toluene at 295 K at the molar ratios x = [H_2PyP]/[Quantum dot]: (*1*) 0.0, (*2*) 0.4, (*3*) 0.8, (*4*) 1.2, (*5*) 1.6, (*6*) 2.0, (*7*) 2.4 and (*8*) 2.8.

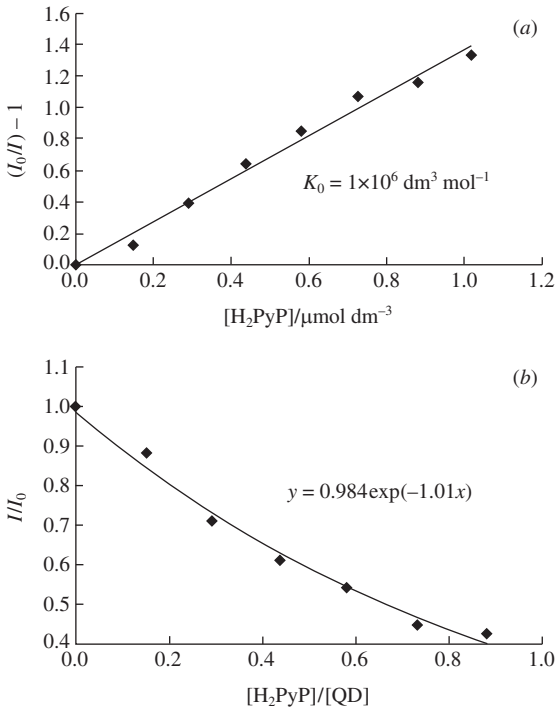


Figure 2 (*a*) Stern–Volmer function of the concentration [H_2PyP] (quantum dot saturation curve) and (*b*) dependence of the relative intensity of the luminescence of quantum dots on the ratio [H_2PyP]/[QD] approximated by the exponential function $I/I_0 = \exp(-x)$.

For evaluating the stoichiometry of the quantum dot–porphyrin complexes, we used a model[17] of the formation of quantum dot–organic molecule complexes. In terms of this model, Figure 2(*b*) shows the dependence of the relative luminescence intensity of quantum dots (I/I_0, where I and I_0 are the quantum dot luminescence intensities in the presence and in the absence of H_2PyP, respectively) on the relative concentration of porphyrin ([H_2PyP]/[QD], where [H_2PyP] and [QD] are the concentrations of porphyrin and quantum dots, respectively). By the approximation of the obtained curve, we found the exponential dependence $I/I_0 = \exp(-nx)$, and the exponent was found to be 1. This means that the stoichiometry of the quantum dot–H_2PyP complex is 1:1.[17]

Further, we quantitatively assessed the effectiveness of energy transfer from quantum dots to the porphyrin. In the test system, FRET from quantum dots to H_2PyP can occur because there is a region of overlapping between the luminescence spectra of quantum dots and the absorption spectrum of H_2PyP. The effectiveness of FRET was determined from the following formula:[18]

$$E = [1 + (R/R_0)^6], \quad (2)$$

where R is the distance between the donor and the acceptor, and R_0 is a critical radius, which is determined from the following relationship:

$$R_0^6 = \frac{9000 \ln 10 \kappa^2 \Phi_{OD}}{128\pi^5 n^4 N} \int I_D^n(\nu)\, \varepsilon_A(\nu) \nu^{-4} d\nu, \quad (3)$$

where Φ_{OD} is the quantum yield of donor luminescence in the absence of an acceptor, κ^2 is an orientational factor, $I_D^n(\nu)$ is the quantum spectral density of donor radiation normalized to unity [$\int I_D^n(\nu)\, d\nu = 1$], $\varepsilon_A(\nu)$ is the molar absorption coefficient of the acceptor, ν is the wave number, and N is Avogadro's number.

According to Visser *et al.*,[19] we calculated the overlap integral of the luminescence spectra of quantum dots and the absorption

spectrum of H_2PyP, which was 2.06×10^{-14} dm^3 mol^{-1} cm^3. The value of κ^2 was 2/3. The critical radius was R_0 = 32.6 Å, as calculated by formula (3). Assuming that the distance from the porphyrin molecule to the quantum dot lies in a range from 23.5 to 25 Å,[17] we found that the effectiveness of FRET (E) in the quantum dot–H_2PyP complex varied from 87.7 to 83.3% according to formula (2).

Thus, we found that the luminescence of the CdSe donor in the quantum dot–H_2PyP noncovalent assemblies in an organic solvent is quenched by the asymmetrical long-chain porphyrin and energy transfer from CdSe to the organic chromophore can efficiently occur by the FRET mechanism. This opens prospects for the design of new donor-acceptor systems for applications as sensors, catalysts, photovoltaic materials, *etc*.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2014.06.021.

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