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Highly solvatochromic fluorescence of anthraquinone dyes based on triphenylamines

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ABSTRACT

Five donor-acceptor anthraquinone dyes based on phenylamine/triphenylamines with different substituted groups were synthesized by Suzuki reaction in good yields, and the photophysical properties were studied in organic solvents with different polarity. The title dyes exhibited remarkable solvatochromic fluorescence (>190 nm emission shift in polar media), which was derived from intramolecular charge transfer (ICT) character that revealed by DFT/TD-DFT calculation. And large Stokes shifts (210–306 nm) were observed in different organic solvents, along with rich color changes from blue to green, yellow, orange and even purple-red. The Stokes shifts were linearly dependent on the solvent polarity function $E_T(30)$. Interestingly, it was found from the single-crystal X-ray diffraction analysis that dye **3** displayed two different interleaved channel structures, which was seldom seen in organic compounds and could be used as host for complexation potentially. Electrochemical characterization suggested that the different substituted phenylamine groups attached to anthraquinone unit could lead to tunable potentials and energy levels.

1. Introduction

Organic molecules with an electron donor (D) and an acceptor (A) typically possess intramolecular charge-transfer (ICT) characters and are widely used as various optoelectronic devices [1–5]. In addition, such types of structural compounds are also known to exhibit solvatochromic character resulting in the changes of position, shape, and intensity of absorption/emission bands upon various environment polarity, along with the changes of color and brightness [5–11]. Usually, emission spectra are more sensitive than absorption one to solvent polarity. Based on highly environmental sensitivity and good selectivity, the solvatochromic fluorescent dyes have attracted growing interest for promising potential application as sensitive probes to monitor microenvironment/biomolecules [8,12,13]. These dyes are generally highly polar and undergo significant changes of their dipole moment upon excitation, which could be reflected by the spectral shifts and intensity changes (enhancement or quenching) [14,15]. Additionally, a bathochromic shift is usually called positive solvatochromism (more common) for ICT compounds and the corresponding hypsochromic shift is denoted as negative one with an increase in solvent polarity [16]. However, many elements should be considered in practical application such as emission wavelength, quantum yield and Stokes shift, which mainly depend on the fluorescence molecule, polarity of the solvent and solvation [15,17]. Also, solvatochromic effects in the visible spectrum region would be beneficial to the application of polar probes. Therefore, a large number of solvatochromic compounds through tuning the groups electron donor and/or acceptor strengths have been designed and developed to meet desired properties and functions.

It is well known that anthraquinones (AQs) as electron acceptors have attracted much attention due to potential applications in biology and pharmaceutics [18–21], anion sensing [21–24], organic photovoltaics [25–27]. Besides being as acceptor, anthraquinones are also the parent substance of many dyes, and lots of solvatochromic fluorescence molecules using anthraquinones as electron-accepter have been investigated [10,28–31]. On the other hand, as a unique and widely accepted donating group, triphenylamines (TPAs) show very good electron donating ability and charge

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transfer feature [9,32,33]. Therefore, it would bring great performance by combining two desirable traits into one molecule.

With this background and aim, five ICT fluorescent dyes were synthesized using anthraquinone as electron acceptor and phenylamine/triphenylamines as electron donor. Solvent effects on fluorescence spectra derived from ICT and emission colors in solvents of different polarity were investigated. Interestingly, Dye **3** exhibited nanometer cavity structure in crystal, which was confirmed by TEM.

2. Experimental section

2.1. Materials and methods

All starting materials were obtained commercially without further purification. Solvents were dried and distilled before used. NMR spectra were collected on a Bruker AVANCE III 400 (400 MHz) spectrometer with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as an internal standard. HRMS (high resolution mass spectrometry) data were performed on a Bruker micrOTOF-QII mass spectrometer. UV–vis spectra, Fluorescence spectra and Infrared spectra were recorded with PE LAMBDA35 spectrometer, F-380 spectrometer and Thermo Nicolet iS5 spectrometer, respectively. Fluorescence lifetime measurements were recorded on Edinburg FLS-980 fluorescence spectrometer using time-correlated single photon counting (TCSPC). The single crystal X-ray diffraction data were obtained by a Rigaku XtaLAB P200 diffractometer. The morphology investigation was conducted using a JEM-2100F transmission electron microscope (TEM) at 200 kV. Cyclic voltammetry experiments were performed on a CHI660E electrochemistry workstation.

2.2. Quantum chemical calculation

All molecular geometries were fully optimized at hybrid Density Functional Theory (DFT) levels by B3LYP functions with 6–31G(d) basis set [34]. Time-dependent density functional theory (TD-DFT) was employed to calculate 10 excitation states and obtain absorption spectra using B3LYP/6-31G (d) basis set. All the calculations were performed on a Gaussian 03 program.

The electronic structures and the frontier molecular orbital (MO) energies of dyes **1**–**5** are illustrated in Fig. 2, and the corresponding TD-DFT results are shown in Fig. 1b and Table 2.

2.3. Synthesis

The synthetic route of anthraquinones bearing phenylamine/triphenylamine moieties **1**–**5** are given in Scheme 1. Triphenylamine derivatives **(6a-6c)** were synthesized by our group. Compounds **7** [35], **10** [36], **12** [37], **13a-13c** [38–40] were prepared according to established procedures. The target compounds were synthesized by Suzuki reaction. All as-synthesized compounds were confirmed by ^1H NMR, ^{13}C NMR spectroscopy, high resolution mass spectroscopy and FTIR spectroscopy. The structure of dye **3** was also verified by X-ray crystallography.

*2.3.1. Synthesis of 4,4'-((4-(9,10-dioxo-9,10-dihydroanthracen-2-yl)phenyl)azanediyl)dibenzaldehyde (dye **1**)*

Compound **7** (0.38 g, 1.0 mmol), **10** (0.44 g, 1.3 mmol), tetrabutylammonium (0.16 g, 0.5 mmol) were dissolved in toluene (40 mL) under argon, and K_2CO_3 (2 M, 2.5 mL) was added. The mixture was stirred at room temperature for 15 min, and then $Pd(PPh_3)_4$ catalyst (0.05 g, 0.04 mmol) was added. The reaction mixture was heated to reflux for 12 h. After cooling, the product was extracted with CH_2Cl_2, washed with water, dried over anhydrous $MgSO_4$. The organic layer was evaporated and the compound was purified by flash chromatography on silica gel column (petroleum ether:ethyl acetate = 10:1 as eluent) to give orange solid 0.28 g, yield: 54.90%, m.p. 182–183 °C. IR (KBr, ν, cm^{-1}): 1694 (C=O), 1673 (C=O); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.93 (s, 2H, CHO), 8.54 (s, 1H, Ar-H), 8.43–8.29 (m, 3H, Ar-H), 8.03 (d, J = 7.9 Hz, 1H, Ar-H), 7.79 (dd, J = 29.8, 8.0 Hz, 8H, Ar-H), 7.29 (dd, J = 17.4, 8.2 Hz, 6H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 190.47 (s), 183.15 (s), 182.73 (s), 151.72 (s), 146.33 (s), 145.55 (s), 136.22 (s), 134.30 (s), 134.14 (s), 134.03 (s), 133.67 (s), 133.59 (s), 132.27(s), 131.98 (s), 131.83 (s), 131.43 (s), 128.96 (s), 128.22 (s), 127.30 (d, J = 3.9 Hz), 126.84 (s), 125.29 (s), 123.39 (s); HRMS(ACPI+): m/z calcd for $C_{34}H_{22}NO_4$ $[M+H]^+$: 508.1549, found: 508.1543.

*2.3.2. Synthesis of 2-(4-aminophenyl)anthracene-9,10-dione (dye **2**)*

Dye **2** was synthesized by a similar procedure to dye **1**, which is different from the literature [41]. After purification by flash chromatography on silica gel column (petroleum ether:ethyl acetate = 4:1 as eluent), red solid (0.21 g) was obtained, yield: 70.23%. m.p. 222–223 °C. IR (KBr, ν, cm^{-1}): 1672 (C=O); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.47 (d, J = 1.4 Hz, 1H, Ar-H), 8.36–8.27 (m, 3H, Ar-H), 7.95 (dd, J = 8.1, 1.5 Hz, 1H, Ar-H), 7.79 (dd, J = 5.5, 3.3 Hz, 2H, Ar-H), 7.58 (d, J = 8.4 Hz, 2H, Ar-H), 6.80 (d, J = 8.4 Hz, 2H, Ar-H), 3.90 (s, 2H, NH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 183.49 (s), 182.86 (s), 147.48 (s), 146.79 (s), 134.08 (s), 133.87 (t, J = 5.4 Hz), 133.71 (s), 131.17 (d, J = 3.3 Hz), 128.76 (s), 128.41 (s), 128.05 (s), 127.19 (d, J = 6.6 Hz), 124.28 (s), 115.41 (s); HRMS(ACPI+): m/z calcd for $C_{20}H_{14}NO_2$ $[M+H]^+$: 300.1025, found: 300.1017.

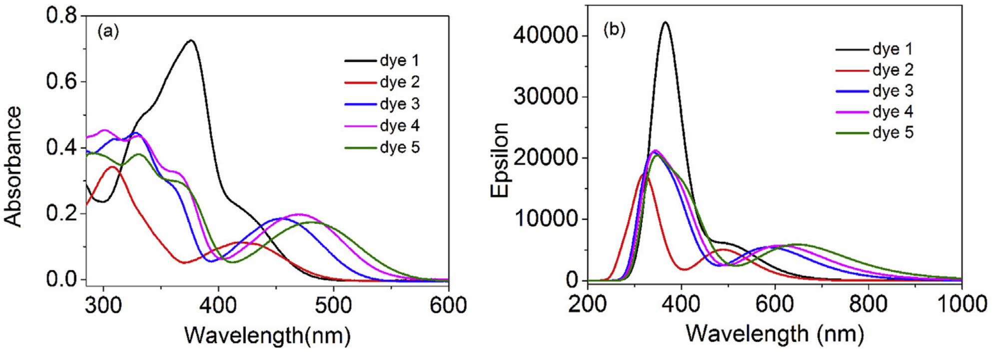

Fig. 1. Experimental UV–Vis absorption spectra of dyes **1**–**5** in toluene (2.0×10^{-5} mol L^{-1}) **(a)** and calculated by TD-DFT at the B3LYP/6-31G(d) level (**b**).