

Cite this: *Chem. Commun.*, 2011, **47**, 4276–4278

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## COMMUNICATION

# Donor–acceptor type silole compounds with aggregation-induced deep-red emission enhancement: synthesis and application for significant intensification of near-infrared photoluminescence†

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Received 5th January 2011, Accepted 15th February 2011

DOI: 10.1039/c1cc00066g

Through efficient Förster resonance energy transfer, the near-infrared emission (850 nm) of a guest (weak near-infrared emitter)–host (strong deep-red emitter) system is greatly enhanced by excitation of the host molecule at 508 nm, in comparison with excitation of the guest molecule at 660 nm.

Luminescent organic materials are fundamentally interesting and practically useful in commercial applications such as organic light-emitting diodes (OLEDs), chemosensors, and bioimaging.<sup>1–3</sup> Although many chromophores are highly luminescent in dilute solutions, the photoluminescence is often quenched in the solid state due to aggregation of their chromophoric units. The aggregation-caused emission quenching (ACEQ) is generally attributed to a nonradiative deactivation process, such as excitonic coupling, excimer formation, and excitation energy migration to the impurity traps.<sup>4</sup> Low bandgap compounds or the donor–acceptor (D–A) type of near-infrared (NIR) chromophores are relatively more prone to ACEQ and usually have low emission efficiency despite their many potential applications.<sup>5</sup> Examples of organic solids that exhibit intense deep-red or NIR emission with high absolute quantum yield are quite limited.<sup>6</sup> Diluting or doping fluorescent compounds in a host material is a common approach to emission enhancement.<sup>7</sup> Another unique approach is based on the discovery made by Tang in 2001 that the luminescence of silole molecules is stronger in the aggregate state than that in solution.<sup>8</sup> A variety of other luminogens, such as distyrylbenzene, fluorene, pentacene, and pyrene derivatives, have also shown the property of aggregation-induced emission enhancement (AIEE).<sup>9</sup> Conceptually, high NIR photoluminescence could be realized by using either the AIEE NIR chromophores if available or using an AIEE chromophore as a host for the ACEQ-type NIR emitters through effective Förster energy transfer.<sup>10</sup>

Nearly all the known AIEE compounds emit the light in the visible region. To realize a red shift of emission into the NIR spectral region, one could introduce an extended  $\pi$ -conjugation or a D–A moiety in a chromophore.

Herein, we report a new series of D–A type silole compounds with aggregation-induced enhancement of deep-red photoluminescence and describe a method for significant enhancement of NIR photoluminescence through an efficient energy transfer from an AIEE host to a weak NIR emitter.

A new series of siloles **2a–e** (Fig. 1) are designed to have a D–A– $\pi$ –A–D structure, in which the central silole unit acts a  $\pi$ -spacer that links the two D–A units and also ensures the AIEE property. The widely used benzothiadiazole group is chosen as an acceptor and attached to several common donors, in order to probe the structure–property relationship. The synthesis of these new siloles requires the use of an intermediate **1**, which was prepared from bis(phenylethynyl)-dimethylsilane and 4,7-dibromo-2,1,3-benzothiadiazole. The silole core (**1**) was then coupled with different donor molecules by the Stille cross-coupling reaction to afford the D–A type silole compounds **2a–e** (Fig. 1). These siloles are all soluble in common organic solvents such as THF, dichloromethane and toluene and fully characterized by spectroscopic methods and elemental analysis (ESI).

The absorption and photoluminescence spectra of **2a–e** were recorded in THF and as solid films (Fig. S7, ESI†). The absorption bands from 300 to 400 nm are attributed to  $\pi$ – $\pi^*$  and  $n$ – $\pi^*$  transitions of the conjugated aromatic segments and those at longer wavelengths are due to the intramolecular charge transfer between the donors and acceptors. An anticipated bathochromic shift was observed with an increase of the electron-donating strength of donors and extension of

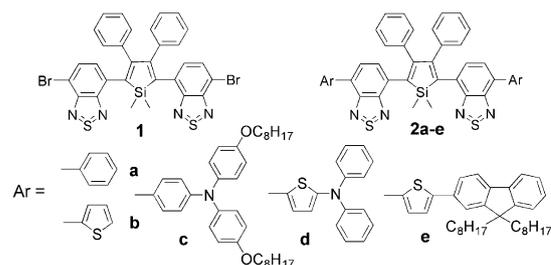
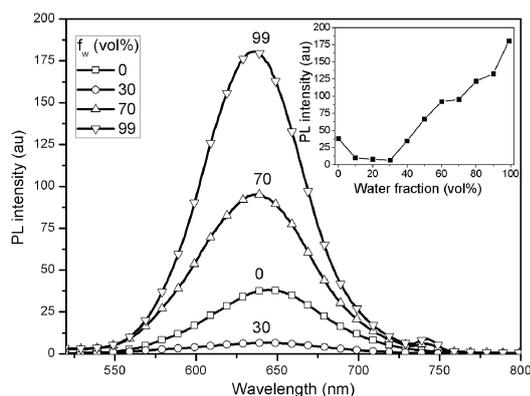


Fig. 1 D–A type silole-based AIEE compounds **2a–e** derived from **1**.

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† Electronic supplementary information (ESI) available: Experimental procedures and characterization data for **2a–2e**, PL spectra of **2b** in the THF–hexane mixtures, and excitation wavelength-dependence study. See DOI: 10.1039/c1cc00066g



**Fig. 2** PL spectra of **2c** in the THF–water mixtures with different water fraction ( $f_w$ ). Inset: correlation between the maximum PL intensity of **2c** and water fraction ( $f_w$ ). Excitation wavelength: 493 nm.

$\pi$ -conjugation length. For example, going from benzene to thiophene donor (**2a** to **2b**) and from thiophene to diphenylaminothiophene donor (**2b** to **2d**), a red-shift of 28 nm (*ca.*  $1384\text{ cm}^{-1}$ ) and 56 nm (*ca.*  $2321\text{ cm}^{-1}$ ) in absorption was observed respectively. In the photoluminescence spectra, compounds without smaller thiophene groups did not have a bathochromic shift in films than in solution, due to the molecules not being coplanar in aggregation to increase the conjugation degree. With the strongest donor among all these siloles, **2d** emits deep red light at 643 nm (in solution) and 666 nm (as film). A further red shift or NIR emission above 700 nm can be expected by introduction of stronger donors and acceptors in this type of silole compounds.

The AIEE property of the siloles **2a–e** is clearly evident by comparison of the photoluminescence in solution and in the solid state (Table 1 and Fig. S6 in ESI). Fig. 2 clearly shows the photoluminescence enhancement of **2c** in THF–water mixture upon addition of a nonsolvent (water) in THF. In THF solution, **2c** emits the red light of 644 nm with a rather low quantum yield of 0.64%. By gradually adding water to its THF solution, **2c** undergo a transition from a solute to aggregate or precipitate. Because the D–A type molecules tend to adopt a more twisted conformation in a more polar solvent, the excited luminogens are in the twisted intramolecular charge transfer state that is susceptible to various nonradiative quenching processes.<sup>4c,11</sup> Therefore, by diluting with water before the formation of aggregates, the PL intensity of **2c**

**Table 1** Absorption and emission properties of **2a–e**<sup>a</sup>

	$\lambda_{\text{max}}^{\text{Abs}}$ [nm]		$\lambda_{\text{max}}^{\text{PL}}$ [nm]		$\Phi_{\text{F}}$ [%] <sup>b</sup>		$\Phi_{\text{F,t}}/\Phi_{\text{F,s}}$
	THF	Film	THF	Film	THF	Film	
<b>2a</b>	436	451	575	575	2.17	10.3	4.8
<b>2b</b>	464	482	573	624	0.17	3.70	21
<b>2c</b>	493	511	644	635	0.64	9.10	14
<b>2d</b>	520	544	643	666	n.d.	1.70	n.d.
<b>2e</b>	501	518	588	635	1.01	2.10	2.1

<sup>a</sup> In THF (10  $\mu\text{M}$ ) and as the film spin-coated on quartz plate.

<sup>b</sup> Fluorescence quantum yield in THF relative to Nile Red ( $\Phi_{\text{F}} = 0.78$ ,  $\lambda_{\text{max}}^{\text{PL}} = 615$  in acetonitrile) and as film determined using an integrating sphere; n.d. = not detectable (signal too weak to be accurately determined).

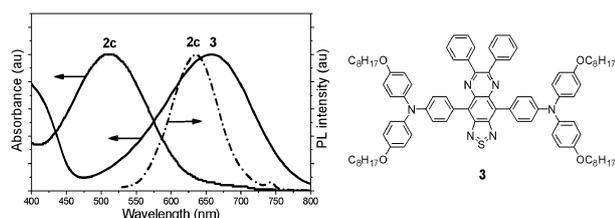
dropped with the water fractions of 30% or less (Fig. 2). At 40% of water fraction or higher, the molecules of **2c** began to aggregate, which results in restriction of intramolecular rotation and the emission enhancement. At 99% of water fraction, the PL intensity was 29 times higher than that at 30% of water fraction. Accordingly, the fluorescence quantum yield of **2c** in the solid film is 14 times higher than that in solution.

All these D–A type silole derivatives have the AIEE property. Although the emission enhancement of **2b** and **2d** is relatively more significant than the others, their fluorescence quantum yields are lower than **2a** and **2c** in the solid state. The low quantum yield is mainly due to a heavy atom effect brought by the thiophene group in **2b**, **2d** and **2e**. The fluorescence quantum yield of **2e** in solution and as a film was quite similar, presumably due to the presence of planar fluorene units for a better  $\pi$ – $\pi$  stacking in film or relatively more PL quenching against the AIEE.

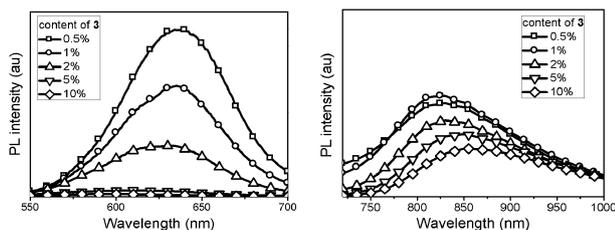
The efficient long-wavelength (635 nm) emission of **2c** in the solid state implies its potential use as a donor chromophore in a guest–host system that may emit the light above 750 nm from an acceptor chromophore through Förster resonance energy transfer.<sup>7b</sup> Accordingly, compound **3** was selected (ESI), with reference to the previously known NIR emitters,<sup>12</sup> because its absorption spectrum overlaps well with the PL spectrum of **2c** in the region of 550–750 nm (Fig. 3). Compound **3** emits weakly above 800 nm in dilute non-polar solvents ( $\Phi_{\text{F}} = 3.7\%$  in toluene) and is totally non-luminous in polar solvents and as a film (Fig. S2, ESI).

Thus, the films on quartz plate were prepared by casting a chloroform solution of a mixture of **2c** containing **3** in an amount of 0.5%, 1%, 2%, 5% and 10% by weight. As shown in Fig. 4, the peak in the visible region is attributed to the emission of the host (**2c**), while the NIR emission comes from the guest (**3**). It should be noted that the emission of **2c** decreased rapidly with increase of the doping concentration of **3**. With 5% of **3** in **2c**, the visible fluorescence was almost completely quenched, indicating an efficient energy transfer from **2c** to **3**. Meanwhile, the NIR emission reached a maximum when the doping concentration increased to 1%. The intensity of the NIR emission gradually decreased with further increase of doping concentration due to the aggregation-caused quenching. The observed red shift in the NIR emission band is also attributed to aggregation of **3** at a higher concentration which leads to enhanced radiative transitions from lower vibronic energy levels.<sup>13</sup>

The excitation-dependent PL of **3** in the film of **2c** was then investigated in order to study and compare the effect of the energy transfer on the NIR emission from **3** (Fig. S3, ESI). First of all, the films of a blend of **2c** and **3** in any ratio only emit weakly at 850 nm when being excited at 660 nm. Secondly, the film of **3** in PMMA also emits weakly when being excited at 660 nm and is not fluorescent at all when being excited at 508 nm where **2c** absorbs intensely (Fig. S5, ESI). Finally, when being excited at 508 nm, the NIR emission of **3** at 850 nm is several times more intense in comparison with excitation at 660 nm for various doping concentrations (Fig. 5). For example, at 1% doping concentration, the NIR PL intensity is enhanced by four times by exciting the host **2c** (508 nm) rather than the guest **3** (660 nm). The results clearly



**Fig. 3** Absorption and PL spectra of the films of host **2c** and guest **3**.



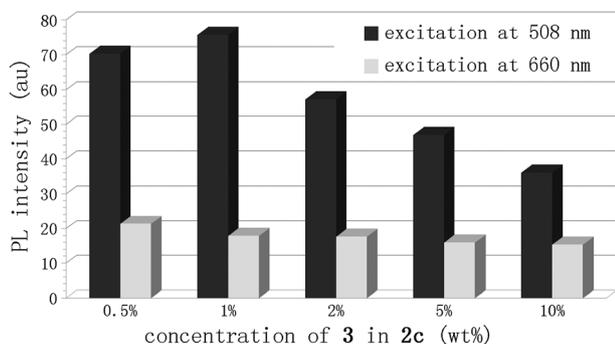
**Fig. 4** PL spectra in the visible (left) and NIR (right) regions of **3** doped in the film of **2c** in different concentrations. Excitation at 508 nm.

indicate that the NIR emission enhancement of **3** in the film of **2c** is attributed to the efficient energy transfer from the AIEE chromophore **2c**. Since molecular diffusion is confined in the solid phase,<sup>10</sup> non-radiative Förster resonance energy transfer is believed to be dominant in the **2c/3** doped system.

The energy transfer from **2b** to **3** was also investigated (Fig. S4, ESI). Similarly, the PL intensity is enhanced by several times by exciting the host **2b** (476 nm) rather than the guest **3** (660 nm). However, the PL of **2b/3** film is weaker than the **2c/3** film under the same test conditions, which is mainly due to a lower fluorescence quantum yield of **2b** than **2c** in the solid state and less spectral overlapping. The PL enhancement of **2d/3** and **2e/3** was not obvious and less significant.

In conclusion, significant enhancement of the NIR emission from a weak NIR emitter **3** doped in the film of **2c** demonstrates an efficient energy transfer in the guest–host system containing the D–A type AIEE donor chromophore and a low bandgap acceptor chromophore and implies a potential application in NIR light-emitting diodes.

This work was supported by the National Natural Science Foundation of China (21074132, 20920102032 and 20834001).



**Fig. 5** PL enhancement at 850 nm of the films of **2c** doped with different amounts of **3** with excitation at 508 nm vs. 660 nm.

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