DOI: 10.1002/ange.201108943

Materials Science

1,4-Bis(diarylamino)-2,5-bis(4-cyanophenylethenyl)benzenes: Fluorophores Exhibiting Efficient Red and Near-Infrared Emissions in Solid State**

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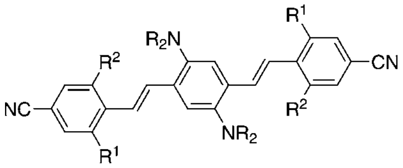
The molecular design and characterization of organic materials exhibiting highly efficient fluorescence in the solid state[1] are some of the urgent research topics supporting advances in optoelectronic devices, such as organic light-emitting diodes (OLEDs),[2] organic solid-state lasers,[3] and fluorescent molecular sensors.[4] Red fluorophores usually consist of planar molecules having extended π conjugation, such as porphyrins and rylenes, or π-conjugated molecules which are substituted with an electron donor (D) and acceptor (A) at the termini of the conjugated system, that is, D–π–A type compounds.[5] Such structural characteristics generally cause strong intermolecular π–π interactions in the densely aggregated state and inevitably consumes the exciton energy, thereby rendering the red fluorophores weakly emissive or non-emissive in the solid state. Red is one of the three primary colors (red, green, and blue) that are essential for the realization of full-color displays and white lighting. In addition, there has been growing interest in π-conjugated compounds that exhibit efficient luminescence in the near-infrared (NIR) region because of their potential applications in bioimaging, night vision devices, and optical communications.[6]

Whereas various chromophores exhibiting efficient NIR fluorescence in solution, such as cyanine dyes, porphyrins, squaraines, benzoheteroles, xanthenes, and borondipyrromethanes (BODIPYs) are frequently developed,[7] organic fluorophores exhibiting efficient solid-state NIR emission are scarcely available owing to much more severe concentration quenching than red fluorophores.[8] Therefore, the development of fluorophores that exhibit efficient solid-state luminescence in the red to NIR region is a challenging and essential first step towards the realization and advancement of solid-state light-emitting devices. We report that the 1,4-bis(diarylamino)-2,5-bis(4-cyanophenylethenyl)benzenes **1**–**3** serve as a new class of fluorophores exhibiting highly efficient solid-state photoluminescence (PL) and whose emission maxima range from orange to the NIR region (Figure 1). Moreover, the electroluminescence (EL) performance of **3b** is presented to demonstrate the high potential of the designed fluorophores as emitters applicable to OLEDs.



1a ($R^1 = H$, $R^2 = H$, R = Ph)
1b ($R^1 = H$, $R^2 = H$, R = 4-tBuC_6H_4)
2a ($R^1 = F$, $R^2 = F$, R = Ph)
2b ($R^1 = F$, $R^2 = F$, R = 4-tBuC_6H_4)
3a ($R^1 = CF_3$, $R^2 = H$, R = Ph)
3b ($R^1 = CF_3$, $R^2 = H$, R = 4-tBuC_6H_4)

Figure 1. Structures of 1,4-bis(diarylamino)-2,5-bis(4-cyanophenylethenyl)benzenes **1**–**3**.

The D–π–A system is an attractive electronic structure for organic light-emitting materials because the photophysical and redox properties can be fine-tuned by the judicious combination of a donor and an acceptor.[9] However, push-pull type molecules frequently encounter severe emission quenching in the solid state owing to dipole-induced intermolecular interactions. For example, a neat film of 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4*H*-pyran (DCM), which was a standard red dopant for OLEDs, reportedly exhibited PL with an emission maximum at $\lambda = 665$ nm and a quantum yield of only 0.05.[10] One possible solution to the intrinsic issue of quenching in D–π–A systems is the construction of a linear π-conjugated molecular framework consisting of a D–π–A–π–D electronic structure, wherein the dipoles originating from the left and right halves of the symmetrical molecule cancel out because of antipar-

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[**] This work was supported by Grants-in-Aid for Creative Scientific Research (No. 16GS0209), and Scientific Research (No. 22350081) from the Ministry of Education, Culture, Sports, Science and Technology (Japan), and the Adaptable and Seamless Technology Transfer Program (No. AS2211079D) from the Japan Science and Technology Agency.

allelism. Successful examples of red-emitting materials of the type D–π–A–π–D include diarylamino-terminated 1,5-dicyano-2,6-bis(styryl)naphthalenes,[11] bis(1-cyano-2-arylethenyl)benzene,[12] diarylfumaronitriles,[13] dithienylbenzo-[1,2,5]thiadiazole,[14] and dimesitylboryl-substituted quaterthiophene.[15] In contrast, the design and development of red-emissive organic solids consisting of the A–π–D–π–A framework, which is an electronic counterpart of the D–π–A–π–D skeleton, remains unexplored.[16,17] We recently demonstrated that 2,5-bis(2,2-diacetylethenyl)-1,4-dipiperidinobenzene, which could be classified as an A–π–D–π–A fluorophore, exhibited red emission in the solid state with a high quantum yield.[18] However, there was little room for structural modification of the 2,2-diacetylethenyl moiety and piperidyl group to fine-tune the emission color and extend it to the deep-red to NIR region. Then, we designed **1**–**3** to develop new chromophores exhibiting efficient solid-state emission in the red to NIR region on the basis of the molecular design of molecules having a A–π–D–π–A framework.[19]

Compounds **1**–**3** were readily prepared by the double Horner–Wadsworth–Emmons reaction of the corresponding 4-cyano-substituted benzaldehydes with 2,5-bis(diethylphosphonatomethyl)-1,4-dibromobenzene and subsequent palladium-catalyzed *N*-arylation with secondary amines.[20] The decomposition temperatures (T_d) of **1**–**3**, temperatures at which the compounds lose 5 % of their weight, ranged from 316 °C to 377 °C.[20] These data clearly indicate that all the compounds are thermally stable. Such good thermal stability is a desirable characteristic for the purification of materials by vacuum sublimation, fabrication of organic devices by vacuum deposition, and extended device lifetimes.

Single crystals of **1a** suitable for X-ray analysis were obtained by recrystallization from CH_2Cl_2/*n*-hexane. Compound **1a** crystallizes in the monoclinic space group *C*2 without inversion symmetry with respect to the centroid of the central benzene ring.[20,21] The bis(styryl)benzene framework is slightly distorted as the dihedral angles between two 4-$NCC_6H_4CH{=}CH$- moieties and the central benzene ring are 8.5° and 21.3° (Figure 2a). The phenyl group of one amino substituent orients itself above the central benzene plane and the other orients itself below the plane (Figure 2b). There is no π–π stacking between the bis(styryl)benzene skeletons of adjacent molecules, presumably owing to the symmetric electronic structure and the twisted conformation of the bulky amino moieties (Figures 2c and d). This packing mode is beneficial for preventing excimer formation and Dexter-type energy transfer leading to the loss of the excited energy.

The absorption and fluorescence data of compounds **1**–**3** in toluene are summarized in Table 1. The spectra of **1a**, **2a**, and **3a** are shown in Figure 3.[20] Each compound shows a strong absorption band at $\lambda = 334$–353 nm, which is assignable to a π–π* transition, and a weaker band at $\lambda = 456$–498 nm, which can be ascribed to an intramolecular charge-transfer (CT) transition. Fluorescence maxima appeared in the region ranging from yellow to red with large Stokes shifts. There was very little overlap in the absorption and fluorescence spectra, thus suggesting that the designed structures of **1**–**3** were advantageous for suppressing energy transfer through the Förster mechanism, which results in luminescence quenching. The absorption and fluorescence spectra of **1**–**3** in CH_2Cl_2, which are shown in the Supporting Information, also support the intramolecular CT transition from dipole-cancelled ground states.

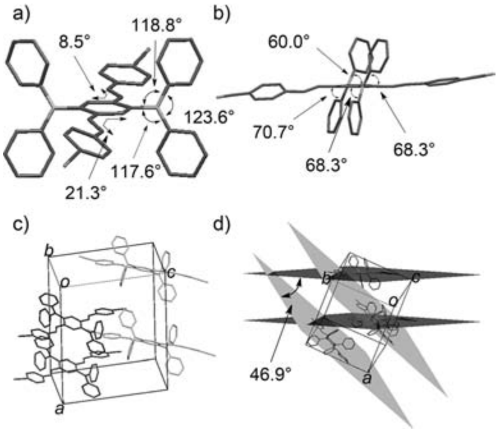

Figure 2. Molecular and crystal structures of **1a**: a) View from a long axis of the molecule, b) side view, c) packing diagram, and d) packing diagram with mean planes of each central benzene ring. Hydrogen atoms are omitted for clarity.

Table 1: Photophysical properties of **1**–**3**.

Cmpd	λ_{abs} [nm][a,b] (ε)[c]	λ_{em} [nm][d] (Φ_f)[e] Solution[a]	Powder	PS film[f]
1a	456 (7200)	565 (0.61)	576 (0.56)	563 (0.75)
1b	471 (5000)	596 (0.55)	605 (0.58)	573 (0.70)
2a	473 (4500)	609 (0.57)	619 (0.20)	591 (0.70)
2b	471 (7600)	643 (0.38)	634 (0.33)	620 (0.58)
3a	473 (3400)	622 (0.53)	667 (0.36)	611 (0.72)
3b	498 (4000)	657 (0.38)	702 (0.33)	643 (0.57)

[a] 1×10^{-5} M in toluene. [b] Absorption maximum at the longest wavelength. [c] Molar absorption coefficient [$M^{-1}cm^{-1}$]. [d] Emission maximum upon photoexcitation at $\lambda = 400$ nm. [e] Absolute quantum yield determined with a calibrated integrating sphere system. [f] A polystyrene film doped with **1**–**3**.

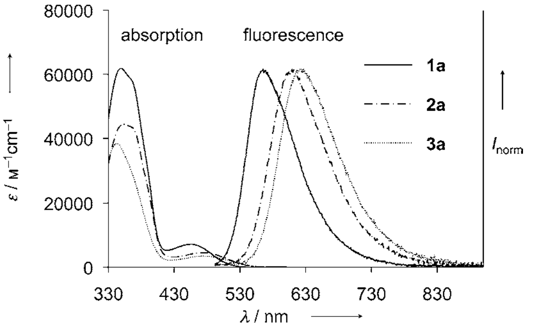

Figure 3. Absorption and fluorescence spectra of **1a**, **2a**, and **3a** in toluene at 1×10^{-5} M.

Compounds **1**–**3** exhibited fluorescence in the orange to NIR region with good to high efficiency, both in powder form and dispersed in a thin film of polystyrene (PS). The fluorescence data are summarized in Table 1 and the spectra

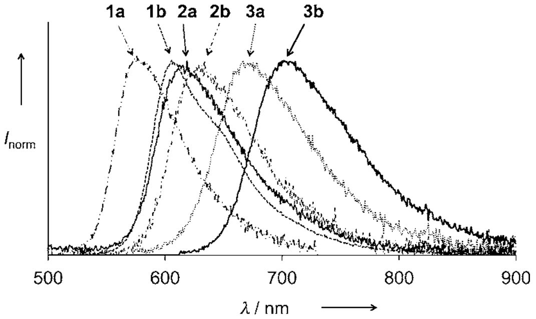

Figure 4. Fluorescence spectra of **1**–**3** as a powder.

of **1**–**3** as a powder are displayed in Figure 4. The emission maxima in powder generally red-shifted compared with those in toluene except for **2b**. The red-shifted emission is presumably attributed to the formation of a physical dimer in which transition dipoles of the monomer are arranged either in-line or in an oblique manner,[1e] whereas the reason for the blue-shifted emission of powder **2b** is unclear at present. Red fluorophores in the pure solid state intrinsically tend to cause aggregation, thus resulting in severe concentration quenching, and thus, it is a formidable challenge to obtain quantum yields exceeding 0.3 with regard to red emission from neat organic solids.[1a,5] Therefore, it is noteworthy that **2b** and **3a** in powder form exhibited intense red emissions at $\lambda = 634$ nm and 667 nm with excellent quantum yields of 0.33 and 0.36, respectively. Moreover, **3b** was found to exhibit a highly efficient NIR emission at $\lambda = 702$ nm with a remarkable quantum yield of 0.33.[22] The highly efficient NIR emission was almost retained ($\Phi = 0.30$) even when luminescence was measured using a suspension of powder **3b** in water.[20] This behavior is a very attractive feature for applications in biological imaging because bioimaging is generally performed in aqueous media where organic fluorescent probes are prone to aggregation which results in emission quenching. In addition, the large Stokes shift of **3b** is advantageous for avoiding imaging interference by excitation and scattered light.

Fluorescence maxima of PS films doped with **1**–**3** appeared at longer wavelengths than those for the toluene solutions, and at shorter wavelengths than those of the powder (Table 1).[20] Fluorescence quantum yields of the PS films ranged from 0.57 to 0.75, which were higher than both those of the toluene solution and powder in all cases. These results indicate that **1**–**3** can also be used as dopant emitters.

The energy gap between the HOMOs and LUMOs of **1**–**3** were calculated from the absorption edge, and the energy levels of the HOMOs were determined by cyclic voltammetry. The LUMO energies were estimated from the HOMO–LUMO gaps and HOMO energies because the reduction waves were structureless. The data and cyclic voltammograms are shown in the Supporting Information. All the compounds showed two reversible oxidation waves,[20] thus suggesting that the radical cations of **1**–**3** were stable. The substitution of the *t*Bu groups onto the phenyl rings of the amino moieties significantly raised the HOMO energies, while having little effect on the LUMO energies. In contrast, the introduction of the electron-withdrawing substituents such as fluorine or trifluoromethyl group in the phenyl groups of the styryl moieties greatly lowered the LUMO levels and slightly lowered the HOMO levels. These results suggest that the transition between the S_0 and S_1 states has an intramolecular CT character.

To gain insight into the intramolecular CT character of **1**–**3**, we carried out density functional theory (DFT) calculations (B3LYP/6-31G(d) level) of **1a** using the structure determined by X-ray analysis. The HOMO is primarily localized over the diphenylamino moieties and the central benzene rings, whereas the LUMO is localized over the bis(styryl)benzene framework.[20] These results are consistent with the substituent effects on the energy levels of the HOMO and LUMO. The time-dependent DFT calculations indicate that the absorption band at $\lambda = 452$ nm could be the transition from the HOMO to the LUMO; in other words, the large Stokes shifts leading to the suppression of Förster-type energy transfer are ascribed to the intramolecular CT from the diarylamino moieties to the cyano-substituted styryl moieties.

To verify the high potential of 1,4-bis(diarylamino)-2,5-bis(4-cyanophenylethenyl)benzenes as light-emitting materials for use in optoelectronic devices, we fabricated the OLED devices I–III using **3b** as a nondoped host emitter (device I) and a dopant (devices II and III) by vacuum deposition. The EL performances of the devices are summarized in Table 2, and the emission spectra are shown in Figure 5.[20] The nondoped device I exhibited EL with the emission maximum at $\lambda = 666$ nm, which was much shorter than that of the PL of **3b** as a powder (Figure 5). Vacuum-deposited thin films of **3b** exhibited PL with an emission maximum at $\lambda = 667$ nm and

Table 2: EL performance of devices I–III.

Device[a]	V_{on} [V][b]	λ_{max} [nm][c]	η_c [cd A^{-1}][d]	η_p [lm W^{-1}][e]	η_{ext} [%][f]	CIE (x, y)
I	3.2	666	0.71	0.87	1.36	0.63, 0.36
II	3.7	662	0.91	1.05	1.66	0.64, 0.36
III	3.6	657	1.44	1.38	2.09	0.61, 0.37

[a] For details of device structures, see the Supporting Information. [b] Turn-on voltage at a brightness of 1 cd m^{-2}. [c] Emission maxima. [d] η_c = Maximum current efficiency. [e] η_p = Maximum power efficiency. [f] Maximum external quantum efficiency.

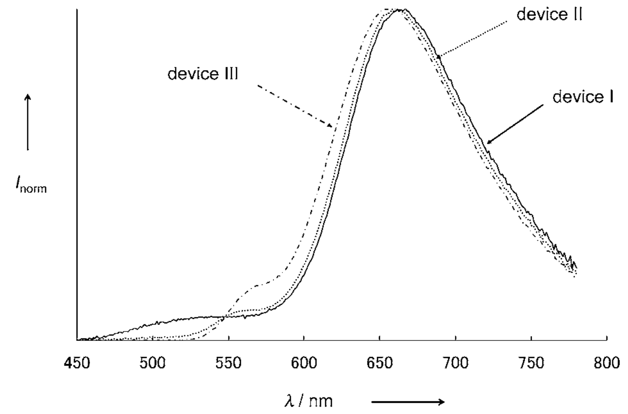

Figure 5. EL spectra of devices I–III.

high quantum yield of 0.28 upon irradiation at $\lambda = 400$ nm.[20] Hence, the blue-shift of the EL compared with the powder PL is ascribed to the morphological difference between the thin film prepared by vacuum deposition and the powder obtained by evaporation of its solution.[23] The PL spectrum and quantum yield of a vacuum-deposited film were constant even when the film was heated at 60 °C for 24 hours.[20] The emission maxima of devices II and III appeared at $\lambda = 662$ and 666 nm, respectively, and were very similar to those of device I and the toluene solutions, thus indicating that the EL emission of all the devices originates from the singlet excited state of **3b**. Small emission bands were observed at around $\lambda = 450$–550 nm in device I, and $\lambda = 500$–570 nm in devices II and III. These bands were attributed to emissions from Alq_3 or rubrene, thus suggesting that the energy transfer from those chromophores was incomplete.[24] Additional optimization of the device configuration is in progress. The external quantum efficiency of the nondoped device I was high (1.36 %)[25] and the efficiency increased to 2.09 % with the doped device III. These preliminary results imply that 1,4-bis(diarylamino)-2,5-bis(4-cyanophenylethenyl)benzenes serve as attractive candidates for light-emitting materials which can be used in nondoped and doped OLEDs, although further studies are necessary for practical applications.

In summary, we have developed 1,4-bis(diarylamino)-2,5-bis(4-cyanophenylethenyl)benzenes as novel fluorophores exhibiting efficient solid-state emission in the region ranging from orange to NIR. The quantum yields in the solid state are good to high, and the emission color can be tuned by changing the substituents on the diarylamino and cyanophenyl moieties. In particular, one of the designed fluorophores exhibited solid-state NIR emission with an excellent quantum yield of 0.33. The long-awaited development of NIR-emissive probes that do not cause aggregation-induced emission quenching in aqueous biological systems is very important in the field of biomolecular imaging, and these results should provide new ideas for the molecular design of efficient NIR-emissive probes. Furthermore, the good EL performance of nondoped and doped devices are presented. These results demonstrate that the molecular design of 1,4-bis(diarylamino)-2,5-bis(4-cyanophenylethenyl)benzenes based on an A–π–D–π–A framework is definitely valid for the invention of organic fluorophores exhibiting highly efficient solid-state emission in the red to NIR region.

Received: December 19, 2011
Revised: February 23, 2012

Keywords: arenes · chromophores · fluorescence · luminescence · materials science

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[20] The Supporting Information includes the preparation and thermal properties of **1**–**3**, the absorption and fluorescence spectra of **1b**, **2b**, and **3b** in toluene and CH_2Cl_2, the optical and fluorescence images of **1**–**3** as a powder, the fluorescence spectra of a suspension of **3b** in water, the fluorescence spectra of **1**–**3** dispersed in a polystyrene film, the electrochemical data and cyclic voltammograms of **1**–**3**, HOMO and LUMO diagrams of **1a**, and the current density-voltage, luminance-voltage, and current efficiency-current density characteristics of devices I–III using **3b**.

[21] CCDC 857967 (**1a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[22] To the best of our knowledge, there are no reported examples on NIR-emissive organic fluorophores whose PL quantum yields in the neat solid state have emission maxima over $\lambda = 700$ nm, except for naphthooxazine derivatives that showed solid-state fluorescence with quantum yields ranging from 0.007 to 0.024 (Ref. [8b]).

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