ORGANIC LETTERS

2008
Vol. 10, No. 2
281−284

Carbazole-Based Donor−Acceptor Compounds: Highly Fluorescent Organic Nanoparticles

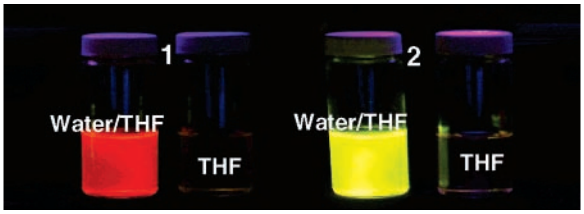
Sujeewa S. Palayangoda, Xichen Cai, Ravi M. Adhikari, and Douglas C. Neckers*

Center for Photochemical Sciences,[1] Bowling Green State University,
Bowling Green, Ohio 43403

neckers@photo.bgsu.edu

Received November 5, 2007

ABSTRACT



Carbazole-based donor−acceptor compounds 1,2-dicyano-*trans*-1,2-bis-4-(carbazolyl)phenylethylene (1) and 1,2-dicyano-*trans*-1,2-bis-4-(3,6-di-*tert*-butylcarbazolyl)phenylethylene (2) were synthesized. 1 and 2 show negative solvatochromic absorption behavior, but show both positive and negative solvatochromic behavior in the fluorescence spectra. In a water/THF mixture, 1 as well as 2 aggregate into 50−150 nm nanoparticles. The emission of nanoparticles of the new types of fluorescent organic nanoparticles (FONs) 1 and 2 is much higher than that of either 1 or 2 in solution

With the wide application of organic light emitting diodes (OLEDs), development of highly efficient emitters is important. Stability and emission in the solid state are important features of organic compounds to be used as OLEDs.[2] However, the substantial emission of compounds in solution usually becomes weak in the solid state due to both intermolecular energy and electron transfer.[3] Therefore, the preparation of compounds that emit efficiently in the solid state is a continuing objective. Donor−acceptor compounds containing an aromatic fumaronitrile core have attracted significant attention as candidates in electroluminescent (EL) devices because of their strong emissions in the solid state.[4,5] Strong emission from 1-cyano-*trans*-1,2-bis-(4′-methylbiphenyl)ethylene (CN-MBE),[3] 2,5-diphenyl-1,4-distyrylbenzene,[6] and 1,4-bis(1-cyano-2-(4-(*N*-4-methoxyphenyl-*N*-phenylamino)phenyl)vinyl)benzene (D-CN)[7] compounds in the solid state has been reported. Either intramolecular planarization or a specific aggregation in the solid state is assumed to be important to the emission in the solid state.[3,8] Such aggregation-induced emissive materials are promising as emitters for the fabrication of highly efficient OLEDs.[9] Interestingly recently discovered fluorescent organic nanoparticles (FONs) are expected to play roles in a wide variety of applications such as nano-sized OLEDs due to the flexibility of synthetic approaches to such compounds.[3] FONs have received a lot of attention,[10,11] and those from perylene and pyrazoline have been reported.[3,12] The emission is related

---

(1) Contribution No. 668 from Center for Photochemical Sciences.

(2) Mondal, R.; Shah, B. K.; Neckers, D. C. *J. Org. Chem.* **2006**, *71*, 4085.

(3) An, B.-K.; Kwon, S.-K.; Jung, S.-D.; Park, S. Y. *J. Am. Chem. Soc.* **2002**, *124*, 14410.

(4) Yeh, H.-C.; Yeh, S.-J.; Chen, C.-T. *Chem. Commun.* **2003**, 2632.

(5) Chen, C.-T. *Chem. Mater.* **2004**, *16*, 4389.

(6) Xie, Z.; Yang, B.; Li, F.; Cheng, G.; Liu, L.; Yang, G.; Xu, H.; Ye, L.; Hanif, M.; Liu, S.; Ma, D.; Ma, Y. *J. Am. Chem. Soc.* **2005**, *127*, 14152.

(7) Kim, D. U.; Paik, S. H.; Kim, S.-H.; Tsutsui, T. *Synth. Met.* **2001**, *123*, 43.

(8) OelKrug, D.; Tompert, A.; Gierschner, J.; Egelhaaf, H.-J.; Hanack, M.; Hohloch, M.; SteinHuber, E. *J. Phys. Chem. B* **1998**, *102*, 1902.

(9) Chen, J.; Xu, B.; Ouyang, X.; Tang, B. Z.; Cao, Y. *J. Phys. Chem. A* **2004**, *108*, 7522.

(10) Kasai, H.; Kamatani, H.; Okada, S.; Oikawa, H.; Matsuda, H.; Nakanishi, H. *Jpn. J. Appl. Phys.* **1996**, *4*, L221.

(11) Kasai, H.; Kamatani, H.; Yoshikawa, Y.; Okada, S.; Oikawa, H.; Watanabe, A.; Itoh, O.; Nakanishi, H. *Chem. Lett.* **1997**, *1181*.

10.1021/ol702666g CCC: $40.75

to the size of FONs with a red-shifted emission resulting from increasing the nanoparticle size.[12]

Herein, we report the synthesis of the carbazole-based donor−acceptor (D-A) compounds, 1,2-dicyano-*trans*-1,2-bis-4-(carbazolyl)phenylethylene (**1**) and 1,2-dicyano-*trans*-1,2-bis-4-(3,6-di-*tert*-butylcarbazolyl)phenylethylene (**2**). These contain the diphenylfumaronitrile core, Figure 1. Formation of **1** and **2** FONs with diameters of 50−150 nm in a THF/water mixture was affected. The quantum yield of emission of **1** and **2** in the solid state is substantially higher than that observed in the solution.

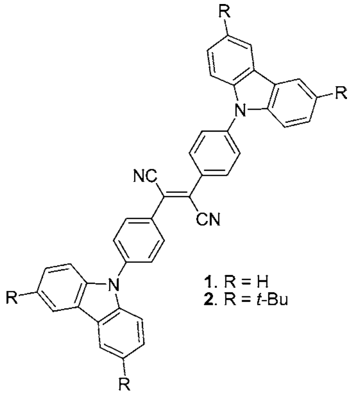
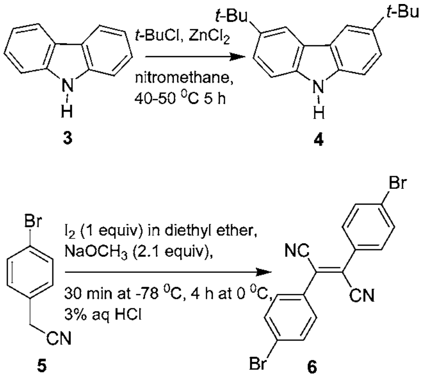


Figure 1. The structures of 1,2-dicyano-*trans*-1,2-bis-4-(carbazolyl)phenylethylene (**1**) and 1,2-dicyano-*trans*-1,2-bis-4-(3,6-di-*tert*-butylcarbazolyl)phenylethylene (**2**).

Diphenylfumaronitrile was utilized as the core because, in the trans form, it consists of antiparallel dipoles. Thus, concentration-related fluorescence quenching in the solid state should be considerably reduced due to dipole−dipole interaction.

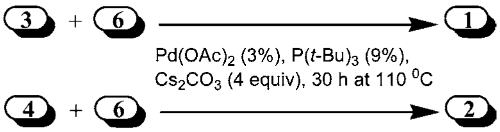
Carbazole deriviatives show high emission quantum yields in the solid state, and the compounds can easily be modified at the 3- and 6-positions of the carbazole to tune the optical properties.[13,14] Carbazole (**3**) was converted into 3,6-di-*tert*-butyl-9*H*-carbazole (**4**)[14] and 4-bromophenylacetonitrile (**5**) was converted into bis(4-bromophenyl)fumaronitrile (**6**)[15] in good yield following literature methods, Scheme 1.

Scheme 1. Synthesis of **4** and **6**



Following a modified literature procedure (Scheme 2) **1** and **2** were synthesized (see the Supporting Information). While compound **1** is red, compound **2** is yellow in the solid state. Both **1** and **2** are stable and dissolve in common organic solvents such as carbon tetrachloride (CCl$_4$), dichloromethane (DCM), tetrahydrofuran (THF), and *N*,*N*-dimethylformamide (DMF).

Scheme 2. Synthesis of **1** and **2**



A change in solvent from nonpolar CCl$_4$ to polar DMF causes a negative solvatochromic shift in the $\pi-\pi^*$ absorption band from 450 to 415 nm for **1** and from 470 to 440 nm for **2**, Figure 2. It is known that solvatochromism depends on molecular structure, the nature of the chromophore, as well as the solvents.[16] Reichardt's pyridinium *N*-phenoxide

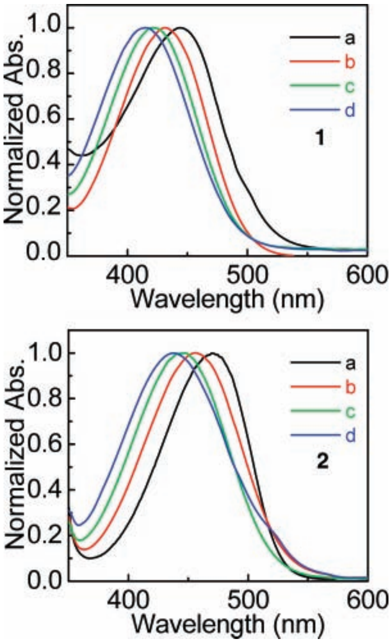


Figure 2. Normalized absorption spectra of **1** and **2** in (a) carbon tetrachloride, (b) dichloromethane, (c) tetrahydrofuran, and (d) *N*,*N*-dimethylformamide.

---

(12) Fu, H.-B.; Yao, J.-N. *J. Am. Chem. Soc.* **2001**, *123*, 1434.

(13) Adhikari, R. M.; Mondal, R.; Shah, B. K.; Neckers, D. C. *J. Org. Chem.* **2007**, *72*, 4727.

(14) Liu, Y.; Nishiura, M.; Wang, Y.; Hou, Z. *J. Am. Chem. Soc.* **2006**, *128*, 5592.

(15) Yeh, H.-C.; Wu, W.-C.; Wen, Y.-S.; Dai, D.-C.; Wang, J.-K.; Chen, C.-T. *J. Org. Chem.* **2004**, *69*, 6455.

(16) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319.

betaine dye and *N*-(*o*-phosphoniobenzylidene)-4-aminophenolate betaine dyes have been reported to show negative solvatochromic behavior.[17] Generally in order for this to be observed, the dipole moment of the molecule in the ground state (μ_g) is expected to be higher than that of the excited state (μ_e).[16] The μ_g of **1** and **2** should be larger than μ_e, because negative solvatochromic behavior was observed, Figure 2.[18]

Interestingly, the emission spectra of **1** and **2** show both positive and negative solvatochromism with increasing solvent polarity, Figure 3. For example, the emission spectrum of **2** was observed with a peak around 580 nm in CCl_4. A broad and red-shifted emission of **2** was observed ($\lambda_{\max}$= 680 nm) in the solvent of medium polarity, dichloromethane. The emission spectrum of **2** was blue-shifted to 520 nm in DMF.

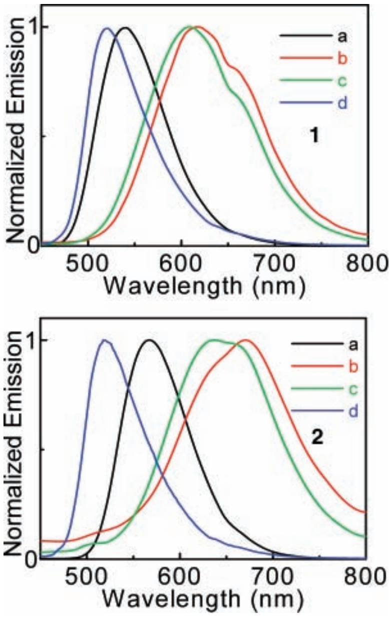


Figure 3. Normalized fluorescence spectra of **1** and **2** recorded in (a) carbon tetrachloride, (b) dichloromethane, (c) tetrahydrofuran, and (d) *N*,*N*-dimethylformamide.

Such inverted solvatochromism has not been observed in fluorescence spectra, although the inverted solvatochromic behavior of the absorption of 4′-hydroxy-1-methylstilbazolium betaine has been reported.[19] A solvent-induced change in the electronic ground state structure results in various solvents.[16] Accompanying structural changes of **1** and **2** in the excited state is intramolecular electron transfer between the carbazole chromophore and the diphenylfumaronitrile core to give **1** and **2** as a charge-separated state.

The excitation spectra of **1** and **2** obtained at 600 nm show that the emission comes from different choromophores in CCl_4, DCM, and DMF (see the Supporting Information).

Excitation spectra of **1** and **2** in CCl_4 are similar to their UV absorption spectra, indicating that the emission mainly comes from **1** and **2** in the singlet excited state (S_1). New absorption bands appear between 300 and 450 nm when **1** and **2** were dissolved in DCM. The 350 nm band became stronger and the 450 nm band became weaker when **1** and **2** were dissolved in DMF.

We submit that intramolecular electron transfer occurs in **1** and **2** caused by a gradual increase in the polarity of the solvents. The quantum yields of emission of **1** and **2** decrease with increasing solvent polarity. In DMF, the charge separation in **1** and **2** is almost complete. Therefore, the emission yield becomes very low.

The markedly enhanced solid-state emision quantum yields of **1** and **2** were measured on a thin film with use of an integrating sphere,[13] Table 1. Park and co-workers observed similar behavior for 1-cyano-*trans*-1,2-bis(4′-methylbiphenyl)ethylene (CN-MBE). In the case of CN-MBE, the polar, bulky cyano group minimizes parallel face-to-face interaction, which induces the H-type aggregation, and this minimizes the fluorescence in the solid state. Since J-type aggregation enhances the emission,[3] **1** and **2** may form J-type aggregates in the solid state.[3,20]

Table 1. Photophysical Properties of **1** and **2**[a]

	$A_{\max}$	$\lambda_{\max}$ (nm)	Φ_{fl}
compound **1**			
CCl_4	445	530	0.37
DCM	435	618	0.07
THF	423	608	0.02
DMF	415	520	<0.01
thin film	455	608	0.72
nanoparticles	453	590	0.70
compound **2**			
CCl_4	470	568	0.44
DCM	457	670	0.01
THF	446	638	<0.01
DMF	440	518	<0.01
thin film	478	553	0.88
nanoparticles	472	550	0.81

[a] Solution quantum yield was calculated with riboflavin (0.30 in ethanol) as a reference. Solid-state quantum yield was measured by using an integrating sphere.

Nanoparticles of **1** and **2** were prepared following a literature method.[3] The red-shifted absorption of **1** and **2** in water/THF (9:1, with nanoparticles) compared to that in water/THF (1:9, without nanoparticles) indicates J-type aggregation occurs with an increasing amount of water (see the Supporting Information). The nanoparticle solutions were transparent and stable. No precipitation was observed on keeping **1** and **2** at room temperature for several months.

The diameters of nanoparticles from **1** and **2** were in the range of 50−150 nm as determined by Scanning Electron Microscopy (SEM), Figure 4 (top). Strong emissions in

---

(17) Allen, D. W.; Li, X. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1099.

(18) Soujanya, T.; Fessenden, R. W.; Samanta, A. *J. Phys. Chem.* **1996**, *100*, 3507.

(19) Jacques, P. *J. Phys. Chem.* **1986**, *90*, 5535.

(20) Yoshika, H.; Nakatsu, K. *Chem. Phys. Lett.* **1971**, *11*, 255.

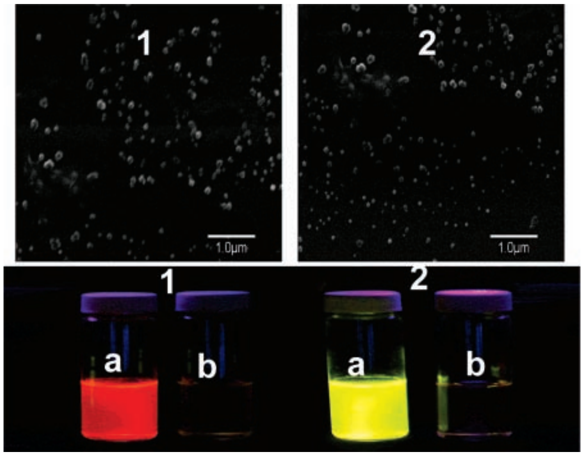


Figure 4. SEM images of **1** and **2** nanoparticles in a water/THF (9:1) mixture (top). The pictures of **1** and **2** taken in a water/THF (9:1) mixture (a) and THF (b) under 365 nm UV light, respectively (bottom). The concentration of **1** and **2** was 1×10^{-5} mol L^{-1}.

water/THF (9:1) can be clearly seen, Figure 4 (bottom), with quantum yields higher than those reported for CN-MBE (0.69) FONs.[3] However, no clear change of particle size was observed on making the particles in solvents differing in the water/THF ratio. We believe that FONs of **1** and **2** with D-A character and high emission will have a number of potential applications in nanosized optoelectronic devices.

In summary, carbazole-based D-A compounds **1** and **2** were successfully synthesized and characterized. The compounds exhibit good stability and solubility in common organic solvents and aggregate to nanoparticles in solvents containing a suitable water/THF ratio. A negative solvatochromism in the absorption spectra of **1** and **2** was observed. Both positive and negative solvatochromic behavior in the emission spectra suggest intramolecular electron transfer in **1** and **2**.

Acknowledgment. The authors greatly appreciate the financial support provided to this work by the Office of Navel Research ONR00014-06-1-0948. We thank Kelechi Anyaogu, our group member, for taking SEM images.

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

OL702666G