Chem. Mater. **2008,** *20,* 6597–6599

Multicolor Emission of Small Molecule-Based Amorphous Thin Films and Nanoparticles with a Single Excitation Wavelength

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Received August 21, 2008
Revised Manuscript Received September 26, 2008

Elaboration of materials emitting multiple colors under single-wavelength excitation drives considerable attention in biomedical imaging[1] and opto-electronics as potential microlasers or emitting displays.[2] The mainstream strategy toward multiplexed emission relies on the use of quantum dots (QDs) of various sizes, which exhibit a broad excitation range and tunable emission.[3] However, their use requires tedious surface functionalization to avoid detrimental emission quenching by charge trapping. Erratic blinking and cytotoxicity of QDs represent additional drawbacks for fast scanning imaging and in vivo applications. Another more recent route involves the association of dyes with distinct absorption and emission spectral ranges giving rise to fluorescence resonant energy transfer (FRET).[1,4] Dyes need to be carefully selected from their photophysical characteristics (spectral overlap, quantum yields, excited-state lifetime) which are usually established in solution. These properties can dramatically differ from those in the solid state, making the selected dyes inappropriate to solid state applications. Moreover, segregation effects causing inhomogeneous dye distribution within the materials can appear due to the largely distinct molecular structures often exhibited by the dyes to ensure broad emission over the entire visible spectrum. One way to address these latter issues would be to obtain push−pull molecular systems where solid-state emission is efficiently tuned by the strength of intramolecular charge transfer (ICT) while their absorption band and main structural backbone remain unchanged. This is often contradictory since both the emission and absorption maxima energetically shift accordingly. This necessarily implies the presence of a second photoactive unit, electronically coupled with the CT excited-state and exhibiting little or no change of its absorption features when increasing the CT extension. To elaborate such systems, we want to take advantage of the strong electronic coupling taking place between the three branches of starburst triarylamines as established from one- and two-photon absorption spectroscopy.[5,6] Surprisingly, although starburst triarylamines, exhibiting strong ICT, have gained indisputable place in electrooptics[7] and biphotonic applications[8] such as optical power limiting,[9] 3D-microfabrication,[10] and bioimaging,[11] unsymmetrical triarylamines whose branches contain interacting photoactive units with specific photophysical signatures, have rarely been investigated.[12] Following these lines, we present herein a novel series of unsymmetrical push−pull triarylamine-based compounds **2**−**5** which form amorphous materials with excellent optical properties and strongly emit from blue to red in the solid state under single UV wavelength excitation through simple tuning of the ICT energy.

To design such molecules, 4-*tert*-butylbiphenyl units were coupled to the electron-donating triphenylamino core substituted by various electron-withdrawing groups following a Suzuki aromatic coupling catalyzed by palladium(0) (Scheme 1).

Their role was twofold: first, to efficiently convey energy toward the lower-energy lying ICT states involving the electron-donor and -acceptor units after UV excitation thanks to their high absorption in the UV range; second, to prevent

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10.1021/cm802264c CCC: $40.75

Scheme 1. Structure of Compounds 1−5

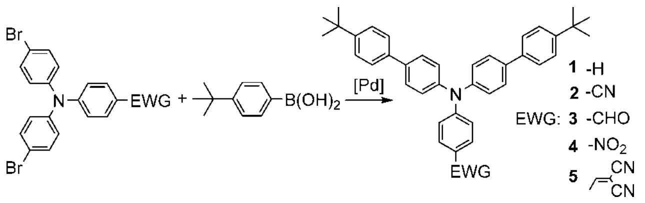

Table 1. Thermal and Optical Properties of Compounds 1−5

	T_g[a] [°C]	μ_{calc} [D]		λ_{max}^{abs} [nm]	λ_{max}^{em} [nm]	ϕ_F[c,d]	σ_{TPA}[e] [GM]
1	68	0.21	C_6H_{12}	328	376	0.73	3
			film[b]	338	383	0.45	115 (NP)
2	94	7.13	C_6H_{12}	331	395	0.42	3.5
			film[b]	336	432	0.81	60 (NP)
3	77	6.20	C_6H_{12}	335, 365	421	0.34	10
			film[b]	340, 377	484	0.39	130 (NP)
4	97	9.03	C_6H_{12}	322, 397	507	0.22	95
			film[b]	324, 415	601	0.15	305 (NP)
5	86	11.29	C_6H_{12}	314, 447	530	0.27	95
			film[b]	319, 479	631	0.20	185 (NP)

[a] DSC analysis: 10 °C·min^{-1} thermal gradient. [b] 100 nm thick evaporated films. [c] Fluorescence standards: 9,10-diphenylanthracene in cyclohexane (ϕ_F = 0.90) for **1**−**3** and coumarine 540A in EtOH (ϕ_F = 0.38) for **4** and **5**. [d] From integration sphere measurements. [e] Measured at 820 nm in cyclohexane or solutions of nanoparticles (NP) dispersed in water with fluoresceine in 0.1 M NaOH as a reference standard.

molecules from deleterious $\pi-\pi$ stacking and get strong emission in the solid state thanks to their bulkiness.[13]

Despite their large dipole moment, compounds **2**−**5** are highly soluble in cyclohexane solution and only exist as amorphous solids as proved by powder X-ray diffraction showing no crystalline feature. Moreover, differential scanning thermal analyses in the 25−300 °C temperature range evidence clear glass transitions around 90 °C with no melting peak or thermal degradation. These glassy properties enable the formation of homogeneous thin films with very smooth surface (rms roughness 2.3 nm over 20 × 20 μm^2) and excellent optical transparency stable over years, by resorting to thermal evaporation under vacuum (9 × 10^{-6} mbar) at 160−180 °C.

All compounds strongly emit in the solid state after excitation in the $\pi-\pi^*$ biphenylamino-located transitions, invariably centered around 330 nm as ascribed from TD-DFT calculations (B3LYP basis/6-31G(d), gas phase, see Supporting Information) or in the lower lying ICT excited states which, in contrast, undergo a bathochromic shift from 336 to 479 nm when increasing the strength of the electron-withdrawing moiety (Table 1). The identical fluorescence quantum yields ϕ_F (0.81 to 0.20 when going from **2** to **5**) obtained for both kinds of excitation, and the spectral match between the excitation and absorption spectra demonstrate the efficient electronic coupling between the biphenylamino-located excited-state S_2 and the emissive ICT excited-state S_1. At this point, it is worth noting the large Stokes shifts (up to 7460 cm^{-1}; $\Delta\lambda$ = 186 nm for film **4**) exhibited by all of the compounds **2**−**5**, which are greatly enhanced in the solid state due to an increase in local polarity compared to cyclohexane solution (Figure 1).[14]

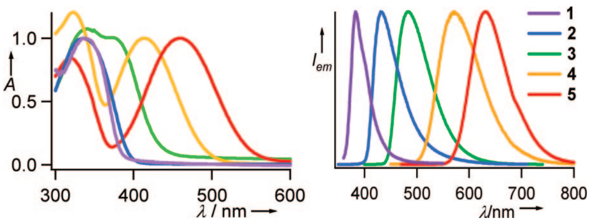

Figure 1. Normalized UV−vis absorption (left) and emission spectra (λ_{exc} = 343 nm) (right) of 100 nm-thick evaporated films **1**−**5**.

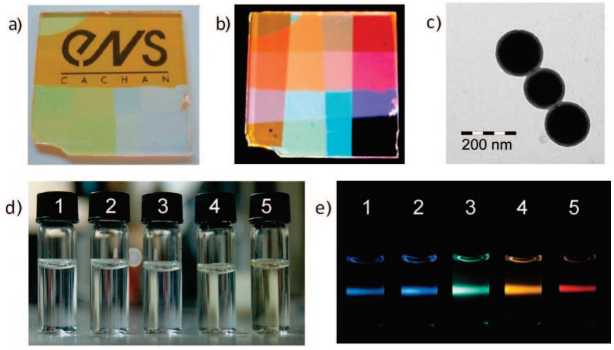

Figure 2. (a) Absorption and (b) fluorescence (λ_{exc} = 365 nm) of multilayered thin films made of successive crossed evaporations of **5**, **4**, **3**, and **2**. (c) TEM image of nanoparticles **5** stained with RuO_4 vapor. (d) Absorption and (e) fluorescence of nanoparticles **2**−**5** dispersed in water (λ_{exc} = 343 nm).

Thus, the combination of large optical Stokes shifts with the UV-absorbing biphenylamino units allowed us to get intense blue to red emission signals peaking from 432 to 631 nm by exciting thin films **2**−**5** with a single wavelength in the UV range (Table 1). To test the ability of an ensemble of compounds **2**−**5** to generate multicolor emission, we elaborated multistacked thin films from successive vacuum thermal deposition of layers **5**, **4**, **3**, and finally **2**.

Thermal evaporation of small molecules gives indeed straightforward access to transparent multilayer thin films with no heating or cross-linking intermediate steps.[15] By contrast, fabrication of multilayer polymer thin films is challenged by the dissolution of existing layers during the deposition of additional ones.[2a,16] Excitation at 365 nm successfully yielded a bright emissive pattern from blue to red with a range of intermediate colors depending on the nature and the order of the deposited layers. To our knowledge, this stacked sample represents the first example of small molecule-based transparent thin film giving multicolor fluorescence after excitation in the UV range (Figure 2a,b).

We eventually explored the multicolor output of compounds **2**−**5** as nanomaterials which are of highest interest for fluo-

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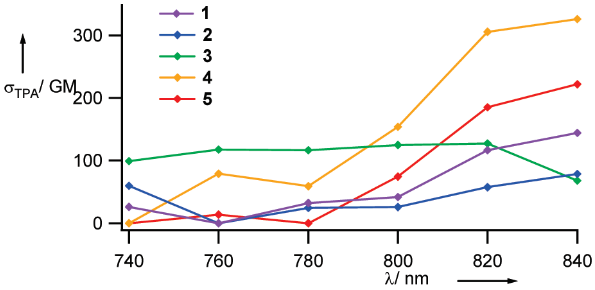

Figure 3. TPA cross sections for nanoparticles **1**−**5** dispersed in water.

rescence imaging applications. Whereas examples of fluorescent polymer[17] or crystalline nanoparticles abound in literature,[18] no attempts to elaborate nanoparticles from small molecules forming exclusively glassy materials appear to have been made. This is all the more surprising since these latter are currently widely used as hole and electron-transport thin layers in organic light emitting diodes.[19]

Nanoparticles were fabricated by the reprecipitation method. Addition of filtered deionized water to a vigorously stirred mixture of the compounds (50 $mg \cdot L^{-1}$) with acetonitrile yields remarkably spherical amorphous particles as evidenced by TEM analysis. Agglomeration or sedimentation was not observed after two months of storage in aqueous solution at room temperature. The nanoparticle diameters were evaluated to be 100−200 nm in agreement with analyses by dynamic light scattering (Figure 2c). The photophysical properties of nanoparticles exactly match those of thin films and present a slight spectral broadening but no additional band compared to solutions. Blue to red emission has again been obtained under single-wavelength excitation at 343 nm in water solution or after deposition on glass coverslips (Figure 2d−e).

Since most of fluorescence imaging finds applications in bioimaging, excitation in the UV can produce undesirable photodamage and autofluorescence of biological materials. By contrast, near-infrared excitation involving biphotonic excitation in the 700−1000 nm spectral range has become extremely popular as it operates in the transparency window of biological tissues.[20] Therefore we examined the two-photon absorption (TPA) of these nanoparticles and found a 5- to 30-fold increase of the TPA cross-sections σ_{TPA} per chromophore compared to those of isoabsorbing cyclohexane solutions (Table 1, Figure 3). Such an enhancement can reasonably be assigned to exciton coupling in the solid state permitted by the high material density and the strong dipolar contribution of the ICT states.[6c,21,22]

Simple calculations considering 200 nm large spherical nanoparticles made of 1 nm sized molecules of **5**, for instance, yields giant TPA cross sections per particle (1.77 × 10^7 GM) superior to those recently reported in dye-doped silica nanoparticles.[23]

This striking result proves that fluorescent organic nanoparticles made of molecules with modest TPA cross sections appear extremely attractive to generate efficient two-photon absorbing systems with little synthetic effort compared to dendrimers containing a high density of TPA chromophores.[24]

In summary, we have devised a new series of unsymmetrical triarylamine derivatives which enable the fabrication of fluorescent amorphous thin films and nanoparticles. The combination of interbranch electronic energy transfer and intramolecular charge transfer allowed us to produce multicolor emission from blue to red under single-wavelength excitation in the UV range. This concept, based on simple molecular structures, opens up perspectives of solid-state emission tuning by simply changing the electronically coupled "branched" chromophores. In addition, we have shown that fluorescent nanoparticles exclusively made of dipolar small molecules can reach unprecedented TPA cross sections above 10^7 GM even though the constituting molecules present modest σ_{TPA}. Such materials should provide an appealing alternative to more complex systems to image biomaterials with a high fluorescence contrast. Their interactions in terms of specificity and magnitude with various biomaterials as well as systematic correlations between the particle size and their optical properties are currently under studies.

Acknowledgment. C. Andraud and O. Maury (ENS Lyon, France) are gratefully thanked for integrating sphere fluorescence measurements.

Supporting Information Available: Synthesis, photophysical properties, two-photon measurements and imaging, and nanoparticle characterizations (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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