

Energy harvesting star-shaped molecules for electroluminescence applications†

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Novel energy harvesting molecules featuring hexaarylbenzene based triarylamine donors and a dithienyl benzothiadiazole acceptor, and that emit red light in electroluminescent devices, have been prepared for the first time.

Energy harvesting molecules with a multi-component architecture in which several chromophores absorb the incident light and channel the excitation energy to a common acceptor core continue to receive considerable attention¹ because they offer attractive artificial models for the natural photosynthetic apparatus. Such light-harvesting systems have already been shown to be useful in multi-electron-transfer catalysis and light-emitting devices.² Energy transfer also plays a very important role in organic light-emitting diodes (OLEDs), particularly OLEDs with red dopants³ and phosphorescent metal complexes.⁴ Recently we found that the building blocks of low bandgap polymers, when encapsulated with appropriate peripheral segments, could effectively lead to fluorophores emitting in the red region.⁵ This site isolation strategy is beneficial for red-emitting chromophores, since they suffer from quantum yield diminishing forces such as aggregation, π - π stacking and dipole-dipole alignment.

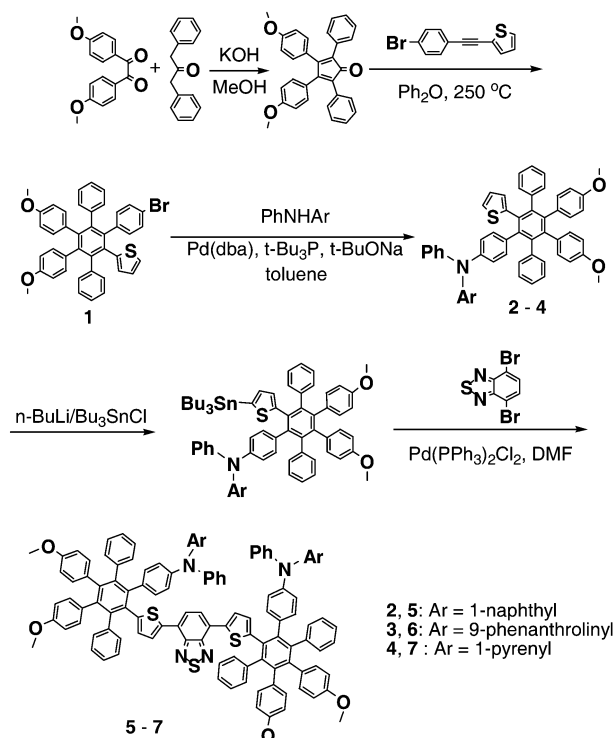
In the present study we introduce a new design that features red emitting dithienylbenzo[2,1,3]thiadiazole⁶ core and star-shaped hexaphenylbenzene decorated with blue emissive arylamine. Rigid, star-shaped molecules are ideal candidates for investigation of energy transfer due to the following reasons: (a) there are fewer tendencies for self-quenching since intramolecular back-folding of the branches and intermolecular aggregation will be suppressed; and (b) there is a well-defined pathway for energy transfer. Among various types of rigid star-shaped compounds, those containing a hexaarylbenzene core appear to have high tendency to form glass with high glass transition temperature.⁷ The present molecules exhibit highly efficient intramolecular energy transfer, bipolar character and bright red emission. Additionally, these molecules were applied as constituent in OLEDs to produce novel orange-emitting electroluminescent devices.

The syntheses of the compounds illustrated in Scheme 1 consist of three key steps: (1) Diels-Alder cycloaddition of 2-(4-bromophenylethynyl)-thiophene with 2,3,4,5-tetraphenylcyclopentadienone to form hexaarylbenzene derivative **1**; (2) palladium catalyzed C-N coupling reaction⁸ of arylbromide (compound **1**) with diaryl amine to give compounds **2-4**; (3) Stille coupling reactions of the tributylstannyl derivatives of **2-4** with 4,7-dibromobenzo[2,1,3]thiadiazole yield compounds **5-7**.⁹ Compounds **2-7** are amorphous once made and possess high glass transition temperatures ($T_g = 123-202$ °C) as well as high thermal decomposition temperatures ($T_d = 404-574$ °C) (Table 1). The relatively higher T_g observed for **5-7** compared to **2-4** arises from *ca.* two-fold higher molecular weight in the former.¹⁰

In the cyclic voltammetry (CV) there is an oxidation wave corresponding to the removal of an electron from the diarylamine. The lower oxidation potential observed for compounds **4** and **7**

(Table 1) may be attributed to the presence of electron rich pyrene unit which helps to stabilize the amine radical cation. In contrast to some red-emitting benzo[2,1,3]thiadiazole derivatives reported recently by us,⁵ the reduction wave due to the central benzo[2,1,3]thiadiazole in **5-7** could not be detected up to -2.0 V.

The absorption and luminescent spectra of the compounds were measured in toluene, and the pertinent data are presented in Table 1. The absorption spectra of the compounds are complex with multiple broad bands. There is a characteristic pyrene $\pi \rightarrow \pi^*$ transition that appears at ~ 400 nm in compounds **4** and **7**; and the 4,7-dithienylbenzo[2,1,3]thiadiazole based transition occurs at ~ 500 nm in compounds **5-7**. Representative absorption spectra are shown in Fig. 1. Compounds **2-4** emit in the purple to blue region, while **5-7** are red emitters. The fluorescence quantum yields in the solution vary from 17-66% in toluene. The independence of λ_{em} on the excitation wavelength supports an efficient downhill energy conversion in compounds **5-7**. There is apparently a strong antenna effect involved in the energy transfer process¹¹ in these systems. The energy transfer should be efficient due to the short distance ($R = \sim 8$ Å) between the donor and the acceptor in these compounds,¹² though internal conversion may occur simultaneously. Energy transfer time, τ_{ET} , calculated from the equation $1/\tau_{ET} = 1/\tau_{dyad} - 1/\tau_{donor}$ for the compounds **5**, **6** and **7** are 2.60, 5.65 and 2.83 ns respectively and in keeping with the distance R . The fluorescence quantum yield of **5** in toluene upon excitation



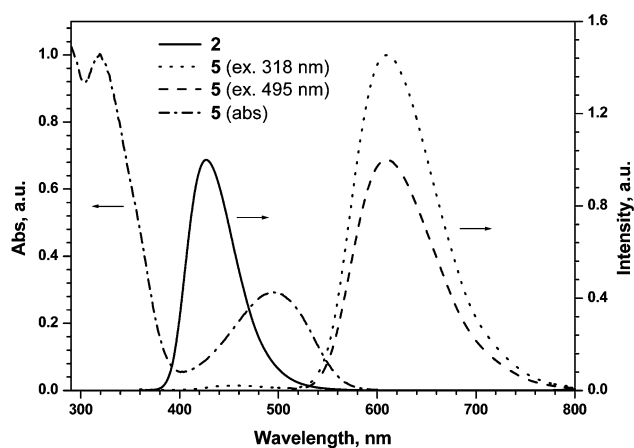
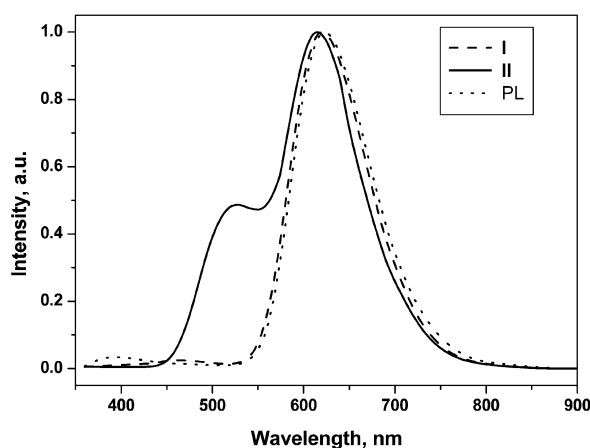
Scheme 1 Synthesis of the compounds.

† Electronic supplementary information (ESI) available: Synthesis and characterization data for the compounds and electroluminescence data. See <http://www.rsc.org/suppdata/cc/b4/b409800e/>

Table 1 Physical and chemical data for 2–7

Compound	$\lambda_{\text{abs}}/\text{nm}^a$	$\lambda_{\text{em}}/\text{nm}$ (Φ_f (%)) ^a	τ/ns	$10^8 k_r^b/\text{s}^{-1}$	$10^8 k_{\text{nr}}^b/\text{s}^{-1}$	$(T_g/T_d)/^\circ\text{C}^c$	$E_{\text{ox}}/\text{mV}^d$	HOMO/LUMO/eV ^e
2	365, 317	428 (17)	1.4	1.2	5.9	123/439	527	5.33/2.06
3	370, 320	428 (20)	1.2	1.7	6.8	141/404	545	5.35/2.08
4	408, 328	463 (45)	1.8	2.5	3.1	146/457	405	5.21/2.32
5	495, 318	609 (64)	0.9	7.0	3.9	182/501	484	5.28/3.05
6	496, 318	610 (66)	1.0	6.7	3.4	195/549	492	5.29/3.06
7	493, 408, 323	612 (63)	1.1	5.7	3.3	202/574	406	5.21/2.97

^a Measured in toluene solutions. Quantum yield (Φ_f , (%)) was measured relative to Coumarin-1 or Nile Red. Corrections due to the change in solvent refractive indices were applied. ^b $k_r = \Phi_f/\tau$; $\Phi_f = k_r/(k_r + k_{\text{nr}})$. ^c T_g and T_d were obtained from DSC and TGA measurements, respectively. ^d E_{ox} was measured in CH_2Cl_2 . All the potentials are reported relative to ferrocene that was used as internal standard in each experiment. Ferrocene oxidation potential was located at +517 mV, with $\Delta E_p = 108$ mV, relative to Ag/AgNO_3 non-aqueous reference electrode. The concentration of the compound was 2.5×10^{-4} M and the scan rate was 100 mV s^{-1} . ^e HOMO and LUMO were calculated from CV data and absorption spectra.

**Fig. 1** Absorption (5) and emission (2 and 5) spectra.**Fig. 2** EL spectra of the devices I and II, and PL spectra for 5.

of the naphthyl units at 318 nm is approximately 1.5 times greater than that observed on direct excitation of 4,7-dithienylbenzo[2,1,3]thiadiazole at 495 nm. However, excitation of **2**, the model compound for **5** without the energy acceptor, at 365 nm results a 428 nm emission. The residual emission from the energy donor in compounds **5–7** is negligible. The excited state life times for the dyads are slightly smaller than the donor molecules. Such intramolecular energy transfer have also been reported for small molecules¹³ and polymers.¹⁴

Despite the high molecular weight, compound **5** can be vacuum deposited as a thin film with retention of film morphology even upon heating at 110°C for >24 h. Devices of different configurations were fabricated for compound **5**: (I) ITO/5 (40 nm)/TPBI (40 nm)/Mg:Ag; (II) ITO/5 (40 nm)/Alq₃ (40 nm)/Mg:Ag; (III) ITO/NPB (40 nm)/5 (10 nm)/TPBI (40 nm)/Mg:Ag (TPBI = 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene; Alq₃ = tris(8-hydroxyquinolinolato)aluminum (III); NPB = 1,4-bis(1-naphthylphenylamino)-biphenyl). The EL spectra of the devices I and III are similar to the PL spectra of the film (Fig. 2), indicating light emission from the compound. In contrast, there is significant emission from Alq₃ in device II. It is likely that the smaller HOMO energy gap between **5** and Alq₃ (HOMO: **5**, 5.28 eV; TPBI, 6.20 eV; Alq₃, 6.09 eV) results in leakage of holes from **5** into the Alq₃ layer. Device I produced a bright red emission with CIE coordinates 0.60, 0.39, maximum brightness of 5320 cd m^{-2} and maximum external quantum efficiency 1.05%. A similar performance was observed for the device III. An attempt was also made using **5** as the electron transport layer. However, the performance of this device was poor, possibly due to the poor electron transport rate of **5**.

In summary, we have synthesized star-shaped donor–acceptor–donor molecules possessing high glass transition temperatures and efficient antenna effect. These materials serve as high T_g EL material. Orange-emitting EL devices have been fabricated, using compound **5** as a hole-transporting/emitting layer, or as an emitting layer.

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