Supporting Information for the submission to the Journal of Materials Chemistry:

Syntheses, Structures, Two-Photon Absorption Cross-Sections and Computed Second Hyperpolarisabilities of Quadrupolar A-π-A Systems Containing *E*-Dimesitylborylethenyl Acceptors

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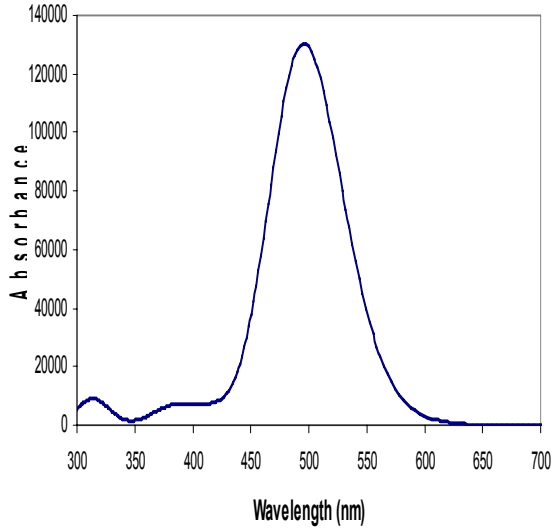
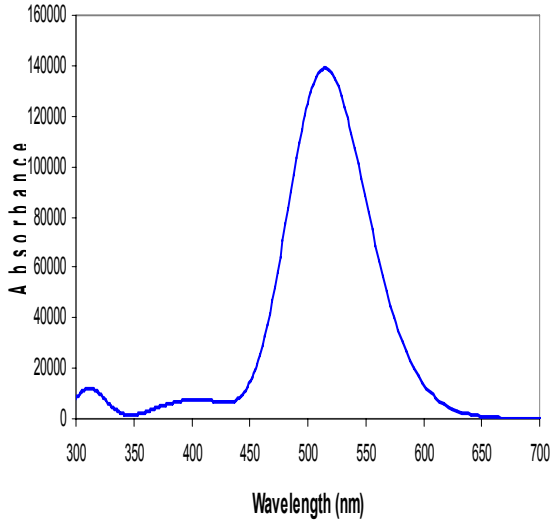
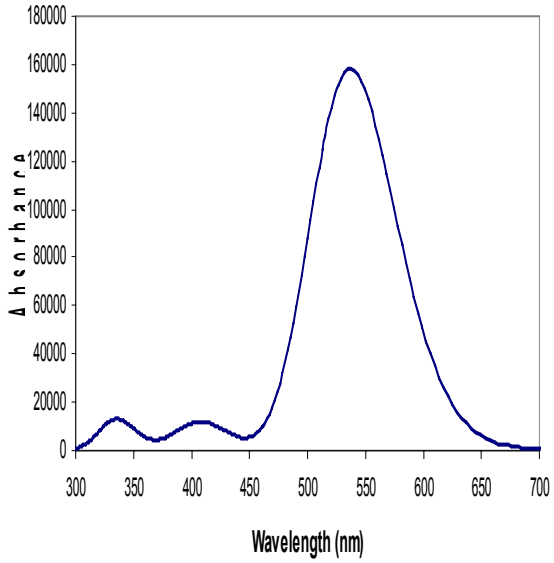


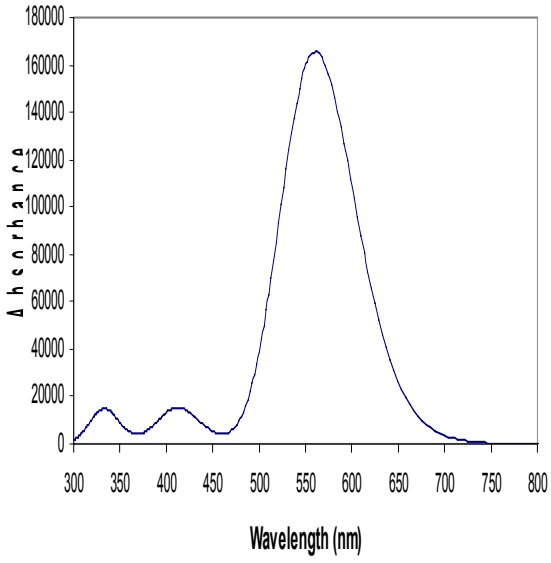
1j



1j (toluene)



1m



1m (toluene)

Fig. S1 TD-DFT computed absorption spectra of compounds **1j** (gas phase, top left, in toluene, top right) and **1m** (gas phase, bottom left, in toluene, bottom right). (Plot using SWizard program, S.I. Gorelsky, http://www.sg-chem.net/swizard/)

Table S1 TD-DFT PBE0/6-31G* energy (λ, nm), oscillator strength (*f*) and composition of the main electronic transitions computed for **1j** and **1m**.[a]

1j (gas phase)[b]	λ (nm)	oscillator strength	transitions[c]
	496	1.8001	H-0→L+0 (80)
	417	0.0611	H-2 →L+0 (87)
	380	0.0624	H-8→L+0 (51) H-6→L+0 (38)
	318	0.0584	H-1 → L+1 (76)
	312	0.0499	H-3 → L+1 (81)
1j (in toluene)			
	515	1.9187	H-0→L+0 (83)
	413	0.0808	H-2→L+0 (89)
	377	0.0385	H-8→L+0 (73)
	316	0.0703	H-1→L+1 (83)
	310	0.0824	H-3→L+1 (82)
1m (gas phase)			
	537	2.1827	H-0→L+0 (81)
	416	0.0184	H-2 →L+0 (72)
	416	0.0338	H-3 → L+0 (72)
	407	0.0993	H-1 →L+0 (53)
	336	0.0992	H-1 →L+1 (84)
1m (in toluene)			
	561	2.2836	H-0→L+0 (84)
	426	0.0398	H-0→L+1 (87)
	410	0.1628	H-3→L+0 (30) H-1→L+0 (29)
	336	0.1073	H-1→L+1 (63)
	331	0.0309	H-2→L+1 (77)

[a] Optimized BP86/6-31G* geometries were used.
[b] For **1j**, a bathochromic shift of 19 nm is observed for the principal band, but all secondary ones show a little hypsochromic shift of ~ 3 nm. [c] Weight of the transition (%).

Absorption and emission spectra of **1j** and **1m** were measured in cyclohexane, toluene, THF, ethyl acetate and dichloromethane, and the λ_{max}(abs) and λ_{max}(em) values obtained in cyclohexane are notably blue-shifted compared to those measured in all other solvents (Table S2). There is no direct correlation between λ_{max}(abs or em) and the solvent dielectric constant, and the shifts are most likely related to specific solvent-solute interactions.

Table S2: Absorption and emission spectroscopic data for **1j** and **1m** in different solvents.

	1j		**1m**	
Solvent	λ_{max}(abs) (nm)	λ_{max}(em) (nm)	λ_{max}(abs) (nm)	λ_{max}(em) (nm)
Cyclohexane	444	491	456	518
Toluene	449	506	469	537
Chloroform	448	505	464	540
Ethyl Acetate	448	503	464	535
THF	448	506	464	540
CH_2Cl_2	448	507	464	542