Supporting Information

Photobehavior and Non−Linear Optical Properties of Push−Pull, Symmetrical and Highly Fluorescent Benzothiadiazole Derivatives

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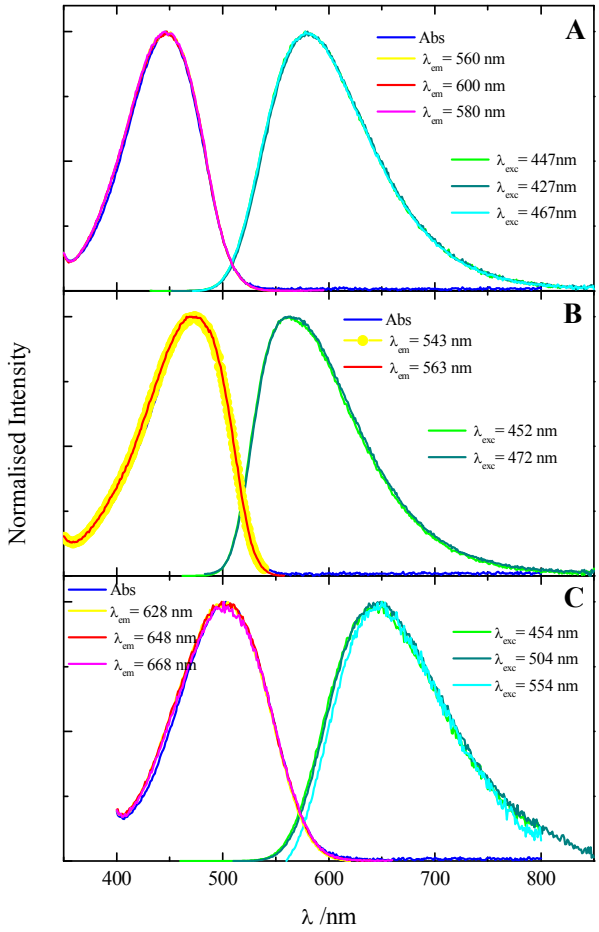

Figure S1. Normalized absorption, fluorescence excitation and emission spectra of **A**–**C** in $CHCl_3$. Wavelength effect on the fluorescence spectra.

Table S1. Full Width at Half Maximum (FWHM) of the emission spectra of **A**–**C** in solvents of different polarity.

Solvent	**f (ε,n²)**	**FWHM / cm⁻¹**		
		A	**B**	**C**
CH	-0.00206	2856		2791
Tol	0.0242	3035	2431	2796
Tol/An 30:70	0.0996	3105	2691	2834
Tol/An 70:30	0.178	3154	3029	2857
An	0.224	3122	3204	2874
$CHCl_3$	0.293	3248	3264	2927
EtAc	0.4000	3221		2896
DCM	0.474	3323	3558	2939
DCE	0.497	3389	3706	2920
DMF	0.6668	3639	4469	2939

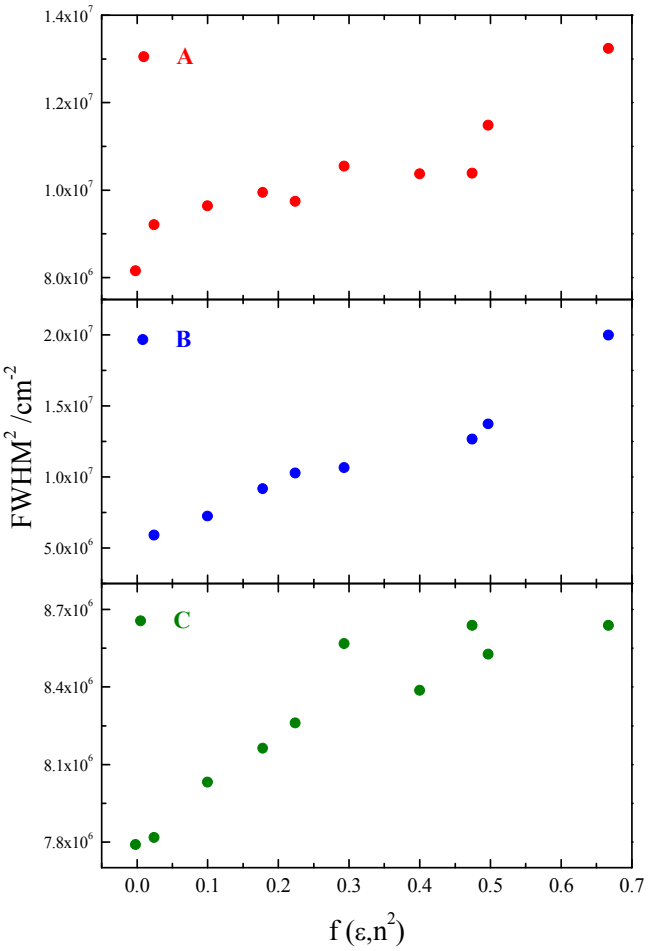

Figure S2. Trends observed for FWHM^2 of the emission spectra of **A**−**C** as a function of f(ε,n^2).

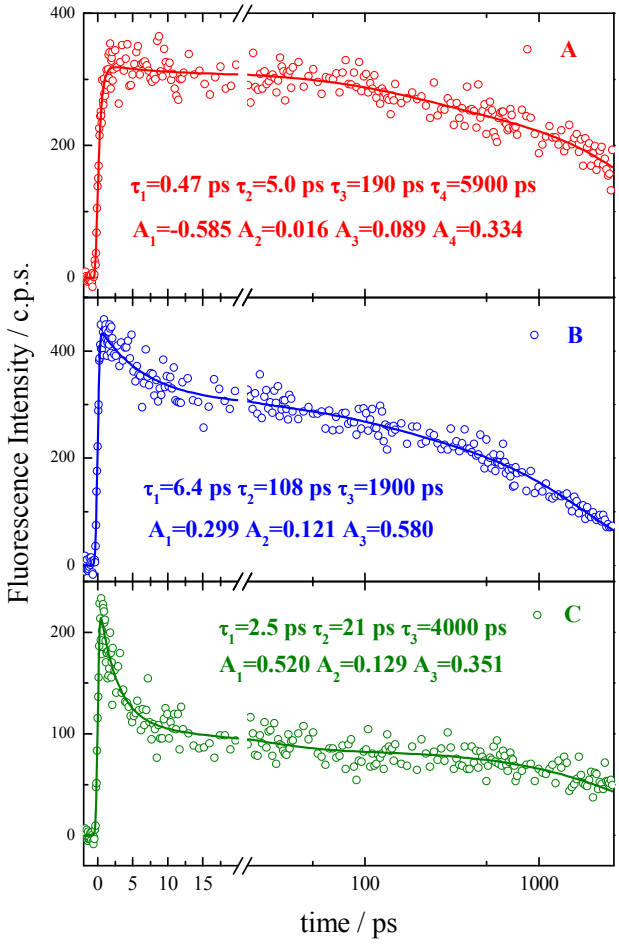

Figure S3. Fluorescence up−conversion kinetics (λ_{exc} = 400 nm) recorded at 575 nm for **A**−**C** in DCE.

Table S2. Excited state kinetic properties of **A**–**C** in solvents of different polarity obtained by ultrafast transient absorption (λ_{exc}=400 nm).

Solvent	τ / ps		
	A	**B**	**C**
Tol	0.29 5.3 2500	0.52 7.4 975 Rest	0.37 6.0 3180
An	0.25 1.8 9.4 2900	0.3 4.4 47 2000 Rest	0.2 2.0 21 2800
$CHCl_3$	0.1 5.6 105 2200	0.1 2.1 29 2100	0.1 3.8 335 4900
DCM	0.5 4.4 64 2250	0.23 3.7 53 3000	0.1 4.8 310 4300
DCE	0.6 4.6 78 2400	0.48 3.0 63 3100	0.17 2.7 146 3400
DMF	0.37 2.2 43 820		0.33 5.0 2700

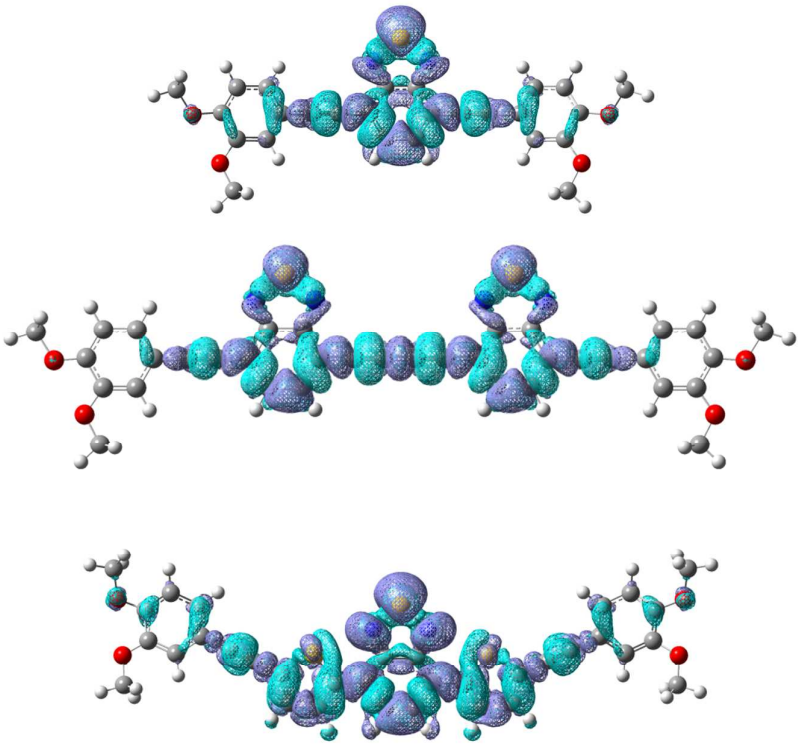

Figure S4. Difference of electron density between states for the $S_0 \rightarrow S_1$ transition of compounds **A**–**C** in DCE (the colours violet and chan correspond to an increase and a decrease in electron density, respectively).

Table S3. Theoretical absorption and emission wavelengths of **A**, oscillator strengths, nature and composition in terms of molecular orbitals obtained by the CAM-B3LYP/6-31G(d) model in DCE (CPCM).

Transition	λ_{th}/nm	f	MO	c_i^2/%	λ_{exp}/nm
$S_0 \rightarrow S_1$	447	1.3790	$\pi_H \rightarrow \pi_L^*$	91	447
$S_0 \rightarrow S_2$	328	0.0000	$\pi_{H-1} \rightarrow \pi_L^*$	86	
$S_0 \rightarrow S_3$	292	1.0186	$\pi_H \rightarrow \pi_{L+1}^*$	68	309
$S_0 \rightarrow S_4$	281	0.3529	$\pi_{H-5} \rightarrow \pi_L^*$	86	
$S_0 \rightarrow S_5$	276	0.1775	$\pi_{H-2} \rightarrow \pi_L^*$	65	
$S_0 \rightarrow S_6$	268	0.0000	$\pi_{H-7} \rightarrow \pi_L^*$	72	
$S_0 \rightarrow S_7$	263	0.0087	$\pi_{H-3} \rightarrow \pi_L^*$	58	
$S_0 \rightarrow S_8$	263	0.0000	$\pi_{H-6} \rightarrow \pi_L^*$	87	
$S_1 \rightarrow S_0$	575	1.3569	$\pi_H \rightarrow \pi_L^*$	95	581

Table S4. Theoretical absorption and emission wavelengths of **B**, oscillator strengths, nature and composition in terms of molecular orbitals obtained by the CAM-B3LYP/6-31G(d) model in DCE (CPCM).

Transition	λ_{th}/nm	f	MO	c_i^2/%	λ_{exp}/nm
$S_0 \rightarrow S_1$	479	2.6856	$\pi_H \rightarrow \pi_L^*$	77	472
$S_0 \rightarrow S_2$	416	0.0001	$\pi_H \rightarrow \pi_{L+1}^*$	49	
$S_0 \rightarrow S_3$	330	0.0251	$\pi_{H-2} \rightarrow \pi_L^*$	45	
$S_0 \rightarrow S_4$	330	0.0002	$\pi_{H-1} \rightarrow \pi_L^*$	42	
$S_0 \rightarrow S_5$	324	0.0000	$\pi_{H-5} \rightarrow \pi_L^*$	82	
$S_0 \rightarrow S_6$	297	0.4372	$\pi_H \rightarrow \pi_{L+2}^*$	32	315
$S_0 \rightarrow S_7$	290	0.0000	$\pi_H \rightarrow \pi_{L+4}^*$	55	
$S_0 \rightarrow S_8$	288	0.1188	$\pi_{H-3} \rightarrow \pi_L^*$	32	
$S_1 \rightarrow S_0$	614	2.8572	$\pi_H \rightarrow \pi_L^*$	87	591

Table S5. Theoretical absorption and emission wavelengths of **C**, oscillator strengths, nature and composition in terms of molecular orbitals obtained by the CAM-B3LYP/6-31G(d) model in DCE (CPCM).

Transition	λ_{th}/nm	f	MO	c_i^2/%	λ_{exp}/nm
$S_0 \rightarrow S_1$	500	1.6621	$\pi_H \rightarrow \pi_L^*$	87	504
$S_0 \rightarrow S_2$	369	0.1295	$\pi_{H-1} \rightarrow \pi_L^*$	71	
$S_0 \rightarrow S_3$	330	1.2570	$\pi_H \rightarrow \pi_{L+1}^*$	63	359
$S_0 \rightarrow S_4$	307	0.1468	$\pi_H \rightarrow \pi_{L+2}^*$	54	
$S_0 \rightarrow S_5$	295	0.0623	$\pi_{H-2} \rightarrow \pi_L^*$	60	
$S_0 \rightarrow S_6$	286	0.3395	$\pi_{H-8} \rightarrow \pi_L^*$	56	
$S_0 \rightarrow S_7$	270	0.1759	$\pi_{H-3} \rightarrow \pi_L^*$	34	
$S_0 \rightarrow S_8$	269	0.0139	$\pi_{H-7} \rightarrow \pi_L^*$	72	
$S_1 \rightarrow S_0$	696	1.6393	$\pi_H \rightarrow \pi_L^*$	94	650

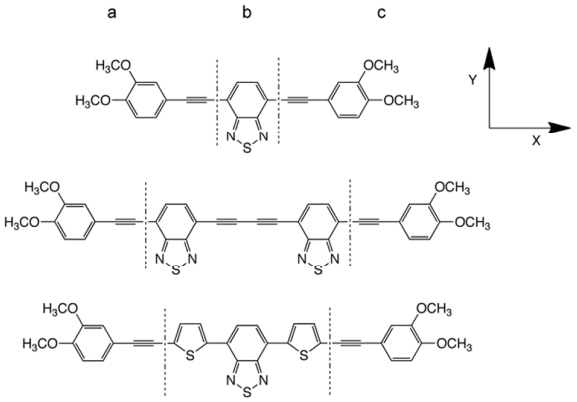

Table S6. Dipole moments (μ, D) together with the Mulliken charges (q) of the **a-c** moieties obtained by the CAM-B3LYP/6-31G(d) model in DCE (CPCM).

compound	state	μ_x	μ_y	μ_z	μ_T	q_a	q_b	q_c
A	S_0	0.00	1.45	0.00	1.45	0.0286	-0.0572	0.0286
	$S_{1,FC}$	0.00	3.41	0.00	3.41	0.0965	-0.1930	0.0965
	$S_{1,rel}$	0.00	4.51	0.00	4.51	0.2032	-0.4064	0.2032
	$S_0@S_{1,rel}$	0.00	3.02	0.72	3.10	0.0582	-0.1164	0.0582
B	S_0	0.00	3.37	0.00	3.37	0.0446	-0.0892	0.0446
	$S_{1,FC}$	0.00	4.92	0.00	4.92	0.0744	-0.1488	0.0744
	$S_{1,rel}$	0.02	5.12	0.00	5.12	0.1446	-0.2891	0.1445
	$S_0@S_{1,rel}$	0.03	3.45	0.00	3.45	0.0728	-0.1454	0.0726
C	S_0	0.00	2.07	0.00	2.07	0.0827	-0.1654	0.0827
	$S_{1,FC}$	0.00	3.26	0.00	3.26	0.1527	-0.3054	0.1527
	$S_{1,rel}$	0.00	3.12	0.00	3.12	0.1640	-0.3280	0.1640
	$S_0@S_{1,rel}$	0.00	1.87	0.00	1.87	0.1016	-0.2032	0.1016

Table S7. Quadrupolar moment Q (field-independent basis, D×Å) of the substrates obtained by the CAM-B3LYP/6-31G(d) model in DCE (CPCM).

comp.nd	state	Q_{XX}	Q_{YY}	Q_{ZZ}
A	S_0	-145	-158	-199
	$S_{1,FC}$	-121	-167	-199
	$S_{1,rel}$	-75	-168	-199
	$S_0@S_{1,rel}$	-136	-158	-199
B	S_0	-159	-227	-277
	$S_{1,FC}$	-139	-233	-277
	$S_{1,rel}$	-75	-233	-278
	$S_0@S_{1,rel}$	-142	-227	-278
C	S_0	-214	-201	-271
	$S_{1,FC}$	-182	-202	-271
	$S_{1,rel}$	-143	-198	-274
	$S_0@S_{1,rel}$	-209	-198	-273

Q_{XY}, Q_{XZ} and Q_{YZ} components display all zero values.

Table S8. Two-photon transition tensor (S) calculated for bianionic Fluorescein (**Fluo**) and compounds **A**-**C** in vacuum by CAM-B3LYP/6-31G* (Dalton).

Sample	Transition	Energy/eV	S_{xx}	S_{yy}	S_{zz}	S_{xy}	S_{xz}	S_{yz}
Fluo	$S_0 \rightarrow S_1$	3.16	38.0	-20.4	-17.6	-18.1	-13.2	-19.1
	$S_0 \rightarrow S_2$	3.63	-29.4	71.0	-8.4	-49.8	-19.4	-2.4
	$S_0 \rightarrow S_3$	3.89	2.4	-1.6	-0.8	-1.6	-0.4	-1.2
	$S_0 \rightarrow S_4$	4.05	0.6	-0.2	-0.3	-0.1	-0.2	-0.3
A	$S_0 \rightarrow S_1$	2.92	0.0	0.0	0.0	47.5	0.0	0.0
	$S_0 \rightarrow S_2$	3.90	-1138.3	9.6	0.2	0.0	0.0	0.0
	$S_0 \rightarrow S_3$	4.34	0.0	0.0	0.0	-100.2	0.0	0.0
	$S_0 \rightarrow S_4$	4.55	0.0	0.0	0.0	-75.0	0.0	0.0
B	$S_0 \rightarrow S_1$	2.70	0.0	0.0	0.0	58.4	0.0	0.0
	$S_0 \rightarrow S_2$	3.17	-485.6	1.0	0.1	0.0	0.0	0.0
	$S_0 \rightarrow S_3$	3.70	0.1	0.0	0.0	0.0	1.7	0.0
	$S_0 \rightarrow S_4$	3.78	-3067.4	9.6	0.1	0.0	0.0	0.0
	$S_0 \rightarrow S_5$	3.86	0.1	0.0	0.0	-75.5	0.0	0.0
	$S_0 \rightarrow S_6$	4.23	0.0	0.0	0.0	-132.1	0.0	0.0
C	$S_0 \rightarrow S_1$	2.58	0.0	0.0	0.0	-9.9	0.0	-0.7
	$S_0 \rightarrow S_2$	3.44	1744.0	0.9	0.0	0.0	-10.3	0.0
	$S_0 \rightarrow S_3$	3.84	0.1	0.0	0.0	-144.5	0.0	1.1
	$S_0 \rightarrow S_4$	4.14	1837.2	-6.6	0.3	0.1	-19.6	0.0
	$S_0 \rightarrow S_5$	4.21	0.6	0.0	0.0	-272.9	0.0	0.0
	$S_0 \rightarrow S_6$	4.43	-66.6	8.8	0.5	0.0	-4.4	0.0