Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Self-Assembly and Mechanochromic Luminescence Switching of Triflurомethyl Substituted 1,3,4-Oxadiazole Derivatives.

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Supporting Information

General procedure of the synthesis of oxadiazole derivatives TFOXD1, TXOXD4, TXOXD6 and TXOXD8: 4-(trifluoromethyl) benzoyl chloride was taken in a dry round bottom flask under argon atmosphere, dry pyridine was added and stirred for 2 mts. The tetrazole derivative was dissolved in pyridine and added drop wise to the above reaction mixture with constant stirring. The reaction mixture was then refluxed at 115 °C for 12 h and poured into ice cold water and then neutralised with 2N HCl. The precipitate was washed with water, filtered and extracted with CH_2Cl_2. The compound was then concentrated and purified by using in hexane-ethyl acetate mixture to give the pure product.

Synthesis of 2-(4-(3,4-dimethoxystyryl)phenyl)-5-(4-(trifluoromethyl)phenyl)-1,3,4-oxadiazole (TFOXD1): Yield = 71%. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS): δ = 8.287–8.271 (d, 2H, *J* = 8 Hz, aromatic), 8.134–8.118 (d, 2H, *J* = 8 Hz, aromatic), 7.820–7.804 (d, 2H, *J* = 8 Hz, aromatic), 7.667–7.650 (d, 2H, *J* = 8.5 Hz, aromatic), 7.218–7.186 (1H, d, *J* = 16Hz, olefinic) 7.115–7.094 (m, 2H, aromatic), 7.035–7.003 (1H, d, *J* = 16 Hz, olefinic),

6.900–6.882 (1H, d, *J* = 9 Hz, aromatic), 3.969 (s, 1H, –OCH_3) and 3.925 (s,1H, –OCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ = 65.10, 163.26, 149.57, 149.23, 141.36, 133.39, 133.13, 131.10, 129.74, 127.41, 127.21, 126.80, 126.14 126.14, 125.34, 121.81, 120.51, 111.24, 108.90, 55.96, 55.91 ppm. MS (HRMS): m/z calcd = 452.43, found 453.14.

Synthesis of 2-(4-(3,4-dibutyloxystyryl)phenyl)-5-(4-(trifluoromethyl)phenyl)-1,3,4-oxadiazole (TFOXD4): Yield = 75% ^{1}H NMR ($CDCl_3$, 500 MHz, TMS): δ = 8.287–8.270 (d, 2H, *J* = 8.5 Hz, aromatic), 8.126–8.109 (d, 2H, *J* = 8.5 Hz, aromatic), 7.819–7.803 (d, 2H, *J* = 8 Hz, aromatic), 7.656–7.640 (d, 2H, *J* = 8.5 Hz, aromatic), 7.197–7.164 (d, 1H, *J* = 16.5 Hz, olefinic), 7.116–7.112 (d, 1H, *J* = 2 Hz, aromatic), 7.083–6.062 (m, 1H, aromatic), 7.011–6.978 (d, 1H, *J* = 16.5 Hz, olefinic), 6.894–6.877 (d, 1H, *J* = 8.5 Hz, aromatic), 4.089–4.026 (m, 4H, –OCH_2–), 1.875–1.797 (m, 4H, –CH_2–), 1.567–1.499 (m, 4H, –CH2–), 1.009–0.978 (m, 6H, –CH_3)ppm. ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 165.13, 163.24, 149.86, 149.34, 141.49, 133.38, 131.25, 129.73, 127.39, 127.20, 126.76, 126.14, 125.12, 124.68, 122.52, 121.70, 120.63, 113.59, 111.77, 69.14, 68.94, 31.40, 31.30, 19.27, 19.24, 13.90, 13.87 ppm. MS (HRMS): m/z calcd = 536.58, found 537.23.

Synthesis of 2-(4-(3,4-bis(hexyloxy)styryl)phenyl)-5-(4-(trifluoromethyl)phenyl)-1,3,4-oxadiazole (TFOXD6): Yield = 65% ^{1}H NMR ($CDCl_3$, 500 MHz, TMS): δ = 8.281–8.265 (d, 2H, *J* = 8 Hz, aromatic), 8.120–8.109 (d, 2H, *J* = 8 Hz, aromatic), 7.815–7.798 (d, 2H, *J* = 8.5 Hz, aromatic), 7.649–7.632 (d, 2H, *J* = 8.5 Hz, aromatic), 7.190–7.157 (d, 1H, *J* = 16.5 Hz, olefinic), 7.109–7.105 (d, 1H, *J* = 2 Hz, aromatic), 7.075–7.055 (m, 1H, aromatic), 7.002–6.970 (d, 1H, *J* = 16 Hz, olefinic), 6.885–6.869 (d, 1H, *J* = 8 Hz, aromatic), 4.0879–4.014 (m, 4H, –OCH_2–), 1.873–1.819 (m, 4H, –CH_2–), 1.514–1.484 (m, 4H, –CH_2–), 1.371–1.341 (m, 8H, –CH_2–), 0.936–0.899 (m, 6H, –CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 165.11, 163.22, 149.85, 149.31, 141.49, 133.37, 131.25 130.52, 129.69, 127.20, 126.89, 126.12, 125.49, 124.68, 122.52, 121.62, 120.63, 113.53, 111.70 69.42 69.21, 31.63, 31.60, 29.32, 29.23, 25.75, 25.71, 22.63, 22.61, 14.03, 14.02 ppm. MS (HRMS): m/z calcd = 592.69, found 593.29.

Synthesis of 2-(4-(3,4-bis(octyloxy)styryl)phenyl)-5-(4-(trifluoromethyl)phenyl)-1,3,4-oxadiazole (TFOXD8) : Yield = 70% ^{1}H NMR ($CDCl_3$, 500 MHz, TMS): δ = 8.282–8.265 (d, 2H, *J* = 8.5Hz, aromatic), 8.120–8.104 (d, 2H, *J* = 8Hz, aromatic), 7.815–7.799 (d, 2H, *J* = 8Hz, aromatic), 7.650–7.633 (d, 2H, *J* = 8.5Hz, aromatic), 7.191–7.158 (d, 1H, *J* = 16.5Hz, olefinic), 7.112–7.109 (d, 1H, *J* = 1.5Hz, aromatic), 7.081–6.061 (m, 1H, aromatic), 7.001–6.977 (d, 1H, *J* = 16.5Hz, olefinic), 6.889–6.872 (d, 1H, *J* = 8Hz, aromatic), 4.077–4.012 (m, 4H, –OCH_2–), 1.872–1.820 (m, 4H, –CH_2–), 1.521–1.467 (m, 4H, –CH_2–), 1.303–1.297 (m, 16H, –CH_2–), 0.905–0.880 (m, 6H, –CH3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 165.11, 163.11, 149.86, 149.32, 141.48, 133.23, 131.25, 129.70, 127.38, 127.19, 126.89, 126.75, 126.10, 125.09, 122.09, 122.52, 121.68, 120.63, 113.56, 111.74, 69.43, 69.23, 31.85, 31.84, 29.42, 29.39, 29.37, 29.31, 29.28, 26.08, 26.04, 22.68, 14.10 ppm. MS (HRMS): m/z calcd = 648.80, found 649.36.

Synthesis of 2-(4-(3,4-bis(hexyloxy)styryl)phenyl)-5-phenyl-1,3,4-oxadiazole (BOXD6): ^{1}H NMR ($CDCl_3$, 500 MHz, TMS): δ = 8.161–8.145 (d, 2H, *J* = 8 Hz, aromatic), 8.120–8.104 (d, 2H, *J* = 8 Hz, aromatic), 7.644–7.627 (d, 2H, *J* = 8.5 Hz, aromatic), 7.562–7.546 (d, 2H, *J* = 8 Hz, aromatic), 7.495–7.463 (t, 1H, aromatic), 7.185–7.153 (d, 1H, *J* = 16Hz, olefinic), 7.111–7.107 (d, 1H, *J* = 2Hz, aromatic), 7.075–6.059 (m, 1H, aromatic), 7.007–6.974 (d, 1H, J = 16.5Hz, olefinic), 6.887–6.870 (d, 1H, *J* = 8.5Hz, aromatic), 4.080–4.015 (m, 4H, –OCH_2–), 1.872–1.818 (m, 4H, –CH_2–), 1.513–1.488 (m, 4H, –CH_2–), 1.385–1.341 (m, 8H, –CH_2–), 0.935–0.898 (m, 6H, –CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ = 165.11, 163.22, 149.85, 149.31, 141.49, 133.37, 131.25 130.52, 129.69, 127.20, 126.89, 126.12, 125.49, 124.68, 122.52, 121.62, 120.63, 113.53, 111.70 69.42 69.21, 31.63, 31.60, 29.32, 29.23, 25.75, 25.71, 22.63, 22.61, 14.03, 14.02 ppm. MS (HRMS): m/z calcd = 524.69, found 524.29.

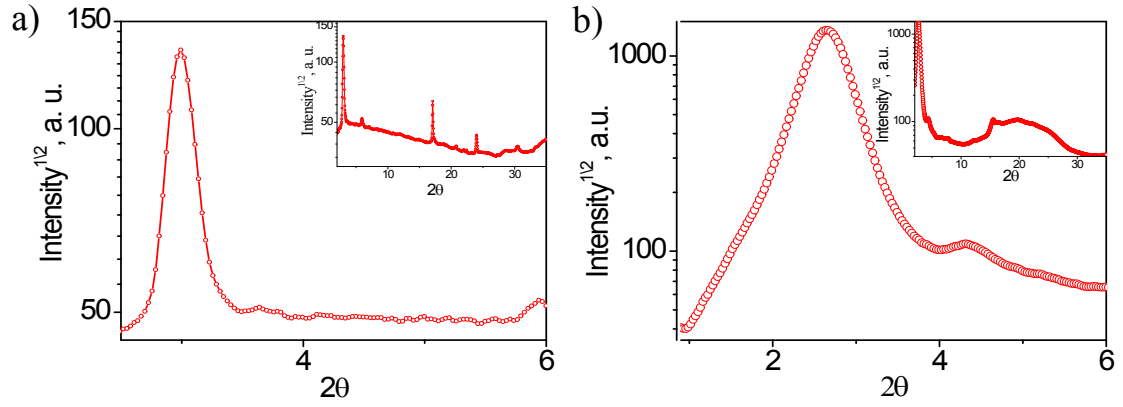

Fig. S1. XRD scans for oxadiazole derivatives. a) TFOXD6 at 114 °C and b) TFOXD8 at 110 °C.

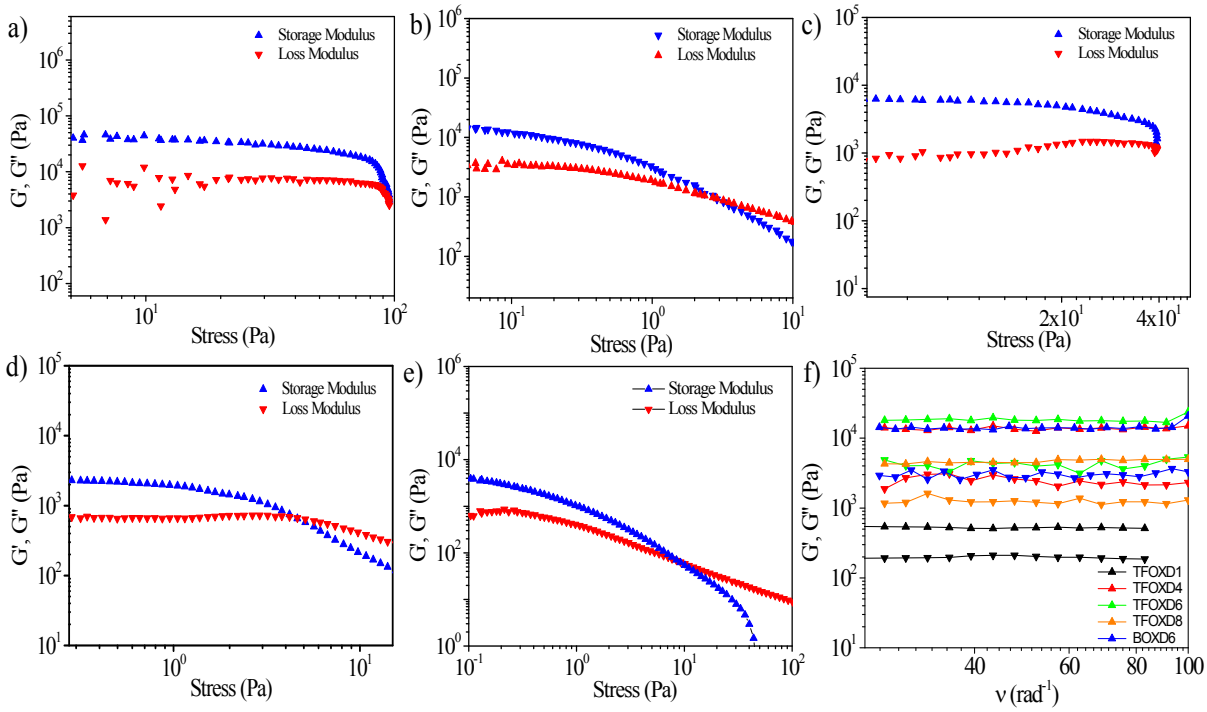

Fig. S2. Dynamic moduli, G' (▲), G'' (▲), vs strain on double logarithmic scale for a gel of oxadiazole derivatives (1 × 10^{-2} M) in *n*–decane at 27 °C; angular frequency, ω = 10 Hz (a TFOXD1, (b) TFOXD4, (c) TFOXD6, (d) TFOXD8 and (e) BOXD6. (f) Dynamic moduli, G' (▲), G'' (▲), *vs*. angular frequency on double logarithmic scale for a gel of oxadiazole derivatives (1 × 10^{-2} M) in *n*–decane at 27 °C.

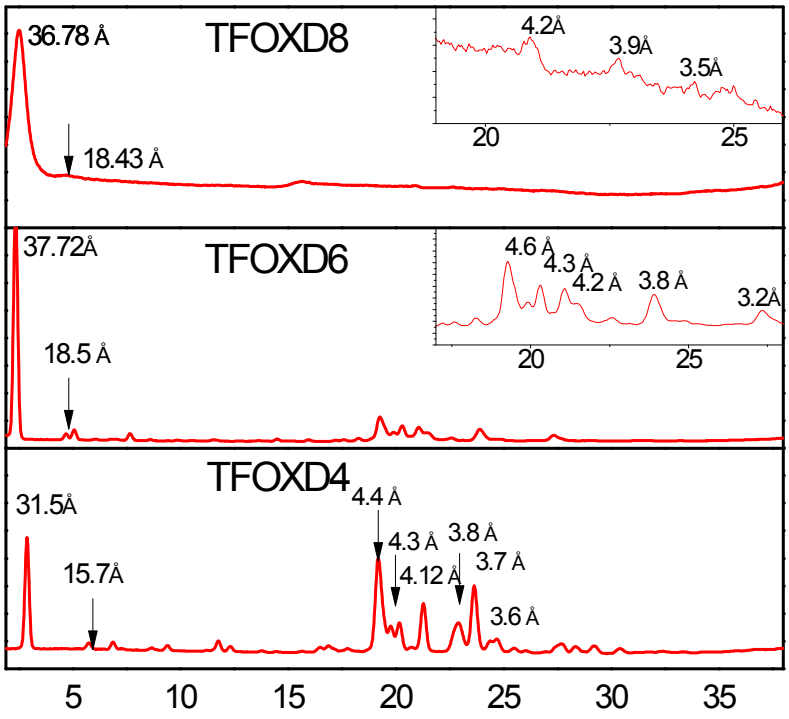

Fig. S3. XRD pattern obtained from the xerogels of oxadiazole derivatives prepared from *n*-decane.

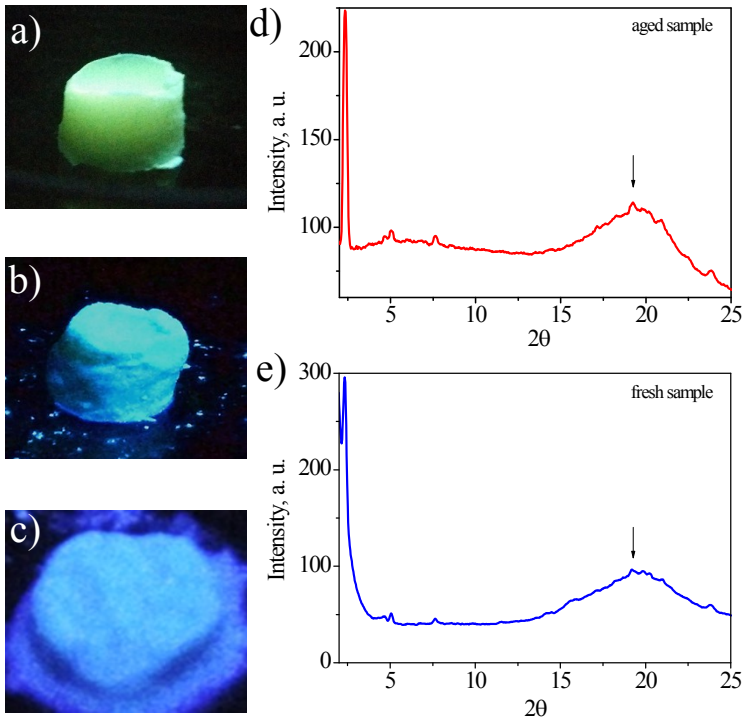

Fig. S4. Photograph showing the emission changes in TFOXD6 gel a) freshly prepared, b) aged and c) after removing the aged surface. XRD pattern of TFOXD6 in gel state d) aged sample and e) fresh sample.

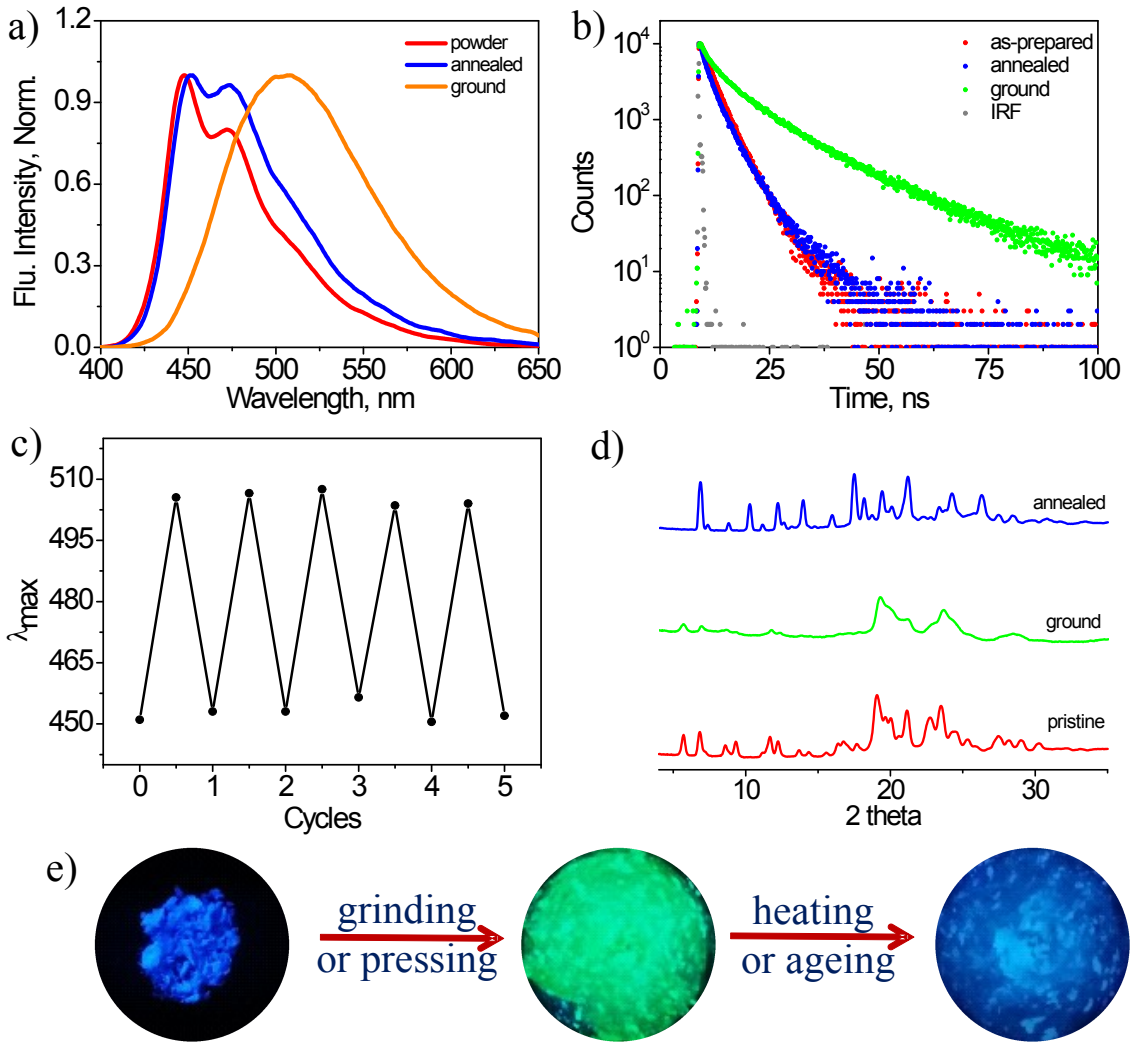

Fig. S5 (a) Fluorescence spectra and (b) fluorescence lifetime decay profile of TFOXD4 in various conditions. c) Reversible fluorescence response over five consecutive cycles of grinding and heating. d) XRD pattern of TFOXD4 at various conditions. (e) The photograph of TOXD4 in various conditions**.**

Table S1. Gelation ability of oxadiazole derivatives in different solvents.

Sample	Decane	Cyclohexane	Methylcyclo-hexane	Toluene	Xylene
TFOXD1	G	P	G	S	S
TFOXD4	G	G	G	S	S
TFOXD6	G	G	G	S	S
TFOXD8	G	S	S	S	S
BOXD6	G	G	G	S	S

G – Gel; P – Precipitate; S – Solution

Table S2. Photophysical properties of oxadiazole derivatives

Sample	Solvent	λ_{max} (nm)	λ_{em} (nm)	ϕ_f	(ns)
TFOXD1	Cyclohexane	362	399, 423, 445	0.64	0.70
	Decane	362	399, 423, 445	0.65	0.71
	Toluene	367	435	0.53	0.65
	Tetrahydrofuran	364	466	0.57	1.19
	Chloroform	364	449	0.44	0.72
	Acetonitrile	359	500	0.19	0.82
TFOXD4	Cyclohexane	360	403, 428, 451	0.68	0.72
	Decane	360	403, 428, 451	0.63	0.75
	Toluene	364	443	0.57	0.69
	Tetrahydrofuran	363	469	0.64	1.26
	Chloroform	363	460	0.49	0.84
	Acetonitrile	361	505	0.18	0.61
TFOXD6	Cyclohexane	363	404, 427, 457	0.70	0.70
	Decane	360	405, 429, 451	0.60	0.75
	Toluene	363	443	0.56	0.70
	Tetrahydrofuran	361	469	0.61	1.27
	Chloroform	362	460	0.46	0.88
	Acetonitrile	360	507	0.17	0.6
TFOXD8	Cyclohexane	362	404,429,451	0.70	0.74
	Decane	363	404, 429, 451	0.70	0.75
	Toluene	367	442	0.60	0.70
	Tetrahydrofuran	362	470	0.70	1.26
	Chloroform	362	460	0.44	0.85
	Acetonitrile	358	504	0.20	0.61
BOXD6	Cyclohexane	360	395, 418, 442	0.68	0.61
	Decane	359	395, 418, 442	0.70	0.63
	Toluene	362	432	0.61	0.60
	Tetrahydrofuran	360	451	0.57	0.65
	Chloroform	362	447	0.51	0.53
	Acetonitrile	355	476	0.22	0.82

Table S3. Photophysical properties of oxadiazole derivatives in gel state.

Sample	Emission max. (nm)	Lifetime					
		τ_1 (ns)	F1 (%)	τ_2 (ns)	F2 (%)	τ_3 (ns)	F3 (%)
TFOXD1	450, 463	0.7	88.6	3.5	11.4	-	-
TFOXD4	450, 470	0.8	30.0	3.4	70.0	-	-
TFOXD6-G	508	1.0	3.96	7.0	39.2	15.2	56.8
TFOXD6-B	453,477	0.7	50.3	2.5	49.7	-	-
TFOXD8	516	1.1	6.0	8.0	33.5	17.1	60.5
BOXD6	464, 483	5.0	76.6	9.6	23.4	-	-

Table S4. Photophysical properties of TFOXD4, TFOXD6 and BOXD6 at various conditions.

Sample		Emission max. (nm)	Lifetime					
			τ_1 (ns)	F1 (%)	τ_2 (ns)	F2 (%)	τ_3 (ns)	F3 (%)
TFOXD4	as prepared	447,472	2.3	63.34	4.6	36.66	-	-
	After grinding	505	1.9	11.86	7	45.42	17.1	42.73
	annealing	450,472	2	60.11	5.2	39.89	-	-
TFOXD6	as prepared	451, 474	2.3	70.9	4.3	29.1	-	-
	After grinding	506	1.5	16.82	6.2	47.68	15.8	35.50
	annealing	451, 474	1.5	65.44	5.5	34.56	-	-
BOXD6	as prepared	450, 481	3	54	8.9	46	-	-
	After grinding	450, 481	5	76	9	24	-	-