Table S1 Crystal structure data for adduct of 1,4-bis(phenylethynyl)-2,5-bis(alkyloxy)benzenes.*

Compound	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**
Empirical formula	C_{12} H9 O	C_{13} H_{11} O	C_{14} H_{13} O	C_{15} H_{15} O	C_{16} H_{17} O	C_{17} H_{19} O
Formula wt	169.19	183.22	197.24	211.27	225.30	239.32
Cell setting	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	P2(1)/c	P2(1)/n	P2(1)/n	P2(1)/n
a (Å)	15.4950(5)	13.0543(5)	5.78560(10)	6.2637(2)	6.2298(2)	6.2970(2)
b (Å)	11.0758(4)	11.0691(4)	14.9764(4)	21.4804(6)	22.1029(6)	22.7824(8)
c (Å)	10.6108(3)	15.2735(5)	13.3619(3)	9.2590(2)	10.0247(3)	10.6411(2)
α (°)	90	90	90	90	90	90
β (°)	102.3920(10)	109.434(2	90.1120(10)	93.187(1)	99.168(2)	105.493(1)
γ (°)	90	90	90	90	90	90
Cell volume ($Å^3$)	1778.59(10)	2081.27(13)	1157.77(5)	1243.84(6)	1362.73(7)	1471.11(7)
Z	8	8	4	4	4	4
F (000)	712	776	420	452	484	516
ρ (g/cm^3)	1.264	1.169	1.132	1.128	1.098	1.081
Crystal size (mm)	0.35 x 0.30 x 0.30	0.35 x 0.30 x 0.25	0.35 x 0.30 x 0.30	0.35 x 0.25 x 0.25	0.35 x 0.35 x 0.20	0.30 x 0.25 x 0.25
No. of measured	6893	12036	15485	12331	14626	5968
No. of independent reflections	1684	1965	2191	2323	2586	2087
Range for data collection θ(°)	2.28 - 25.68	2.56 - 25.69	2.04 - 25.69	2.91-25.65	1.84 - 25.68	1.79 - 23.24
Range of h, k, l	-18 to 18 -12 to 13 -12 to 11	-15 to 15 -13 to 13 -18 to 16	-7 to 6 -18 to 18 -16 to 16	-7 to 6 -26 to 26 -11 to 11	-6 to 7 -26 to 26 -12 to 12	-6 to 6 -25 to 25, -6 to 11
R_1	0.036	0.043	0.042	0.039	0.052	0.045
wR_2	0.091	0.110	0.112	0.099	0.153	0.115
S	1.103	1.026	1.016	1.026	1.113	0.952
No. of parameters refined	154	171	188	205	222	239
Max. $eÅ^{-3}$	0.256	0.120	0.105	0.122	0.254	0.167
CCDC No.	695299	695300	695301	695302	695303	695304

*Crystal data for **C6** has been reported in literature earlier.[17b]

NMR spectroscopic characterizations of 1,4-bis(phenylethynyl)-2,5-bis(alkyloxy) benzenes

1,4-bis(phenylethynyl)-2,5-bis(methoxy)benzenes, **C1**, mp 176-178 °C. ^{1}H NMR (400 MHz, CDCl3): δ 3.89 (s, 6H), 7.03 (s, 2H), 7.34 (m, 6H), 7.57 (m, 4H). ^{13}C NMR: δ 56.66, 85.86, 95.23, 113.57, 115.86, 123.39, 128.50, 128.60, 131.89, 154.10

1,4-bis(phenylethynyl)-2,5-bis(ethoxy)benzenes, **C2**, mp 161-163 °C. ^{1}H NMR (400 MHz, CDCl3): δ 1.38(t, 6H), 4.11(t, 4H), 7.03 (s, 2H), 7.35 (m, 6H), 7.55 (m,4H). ^{13}C NMR: δ 14.91, 65.28, 85.89, 94.87, 114.06, 117.26, 123.04, 128.3, 128.40, 131.6, 153.48.

1*,4-bis(phenylethynyl)-2,5-bis(n-propyloxy)benzenes*, **C3**, mp 153-156 °C. ^{1}H NMR (400 MHz, CDCl3): δ 1.11(t, 6H), 1.87 (m, 4H), 4.00(t, 4H), 7.02 (s, 2H), 7.34 (m, 6H), 7.54 (m, 4H). ^{13}C NMR: δ 10.56, 22.72, 71.12, 85.91, 94.80, 114.02, 117.06, 123.46, 128.23, 128.31, 131.55, 153.62

1,4-bis(phenylethynyl)-2,5-bis(n-butyloxy)benzenes, **C4**, mp 122-124 °C. ^{1}H NMR (400 MHz, CDCl3): δ 1.01, (t, 6H), 1.82, (m, 4H), 1.84 (m, 4H), 4.05 (t, 4H), 7.02 (s, 2H), 7.35 (m, 6H), 7.54 (m, 4H), ^{13}C NMR: δ 13.88, 19.25, 31.37, 69.35, 85.96, 94.80, 114.00, 117.01, 123.48, 128.23, 128.31, 131.55, 153.65.

1,4-bis(phenylethynyl)-2,5-bis(n-pentyloxy)benzenes, **C5**, mp 121-123 °C. ^{1}H NMR (400 MHz, CDCl3): δ 0.93 (t, 6H), 1.43 (p, 4H), 1.56 (m, 4H), 1.86 (p, 4H), 4.04 (t, 4H), 7.02 (s, 2H), 7.35 (m, 6H), 7.54 (m, 4H), ^{13}C NMR: δ 14.06, 22.48, 28.24, 29.03, 69.64, 85.96, 94.81, 113.99, 116.97, 123.47, 128.23, 128.29, 131.55, 153.64.

1,4-bis(phenylethynyl)-2,5-bis(n-hexyloxy)benzenes, **C6**, mp 114-115 °C. ^{1}H NMR (400 MHz, CDCl3): δ 0.80 (t, 6H), 1.35 (m, 8H), 1.57 (m,4H), 1.86 (p, 4H), 4.05 (t, 4H), 7.02 (s, 2H), 7.35 (m, 6H), 7.57(m, 4H). ^{13}C NMR: δ 14.02, 22.62, 25.73, 29.31, 31.59, 69.61, 85.97, 94.81, 113.97, 116.94, 123.47, 128.21, 128.28, 131.55, 153.64.

Table S2: Weak interactions present in the compounds **C1** to **C6**.

Compound	Weak interaction	Distance, (range) H···A	Angle, (range) D-H···A	Number of unique interactions
C1	C-H···π	2.78(2) - 3.04(2)	130.7(2) - 174.4 (2)	8
C2	C-H···π	2.81(1), 3.05(1)	132.7(1),145.7(2)	2
C3	C-H···π	2.73(2), 3.02(2)	135.0(1), 140.6(1)	2
C4	C-H···π	2.79(1) - 2.95(1)	145.0(2),152.6(2)	2
	C-H···O	2.70(1)	144.5(2)	1
C5	C-H···π	2.84(2), 2.88(2)	156.2(2), 140.6(1)	2
C6	C-H···π	2.72(2) - 2.88(1)	132.1(1)- 160.0(1)	3

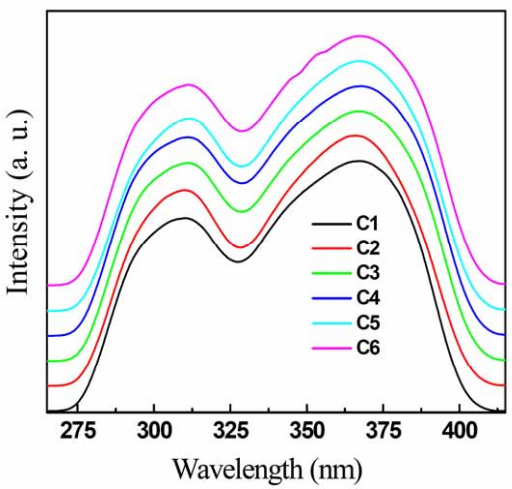

Figure S1. Excitation spectra recorded at 445 nm for the dilute solutions of the alkyloxy substituted (phenyleneethynylene)s in toluene.

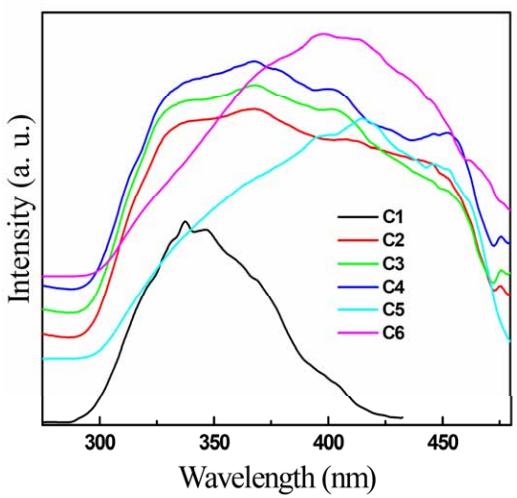

Figure S2: Excitation spectra (emission collected at 480 nm) for the crystals of oligo(phenyleneethynylene)s **C2** to **C6**, Excitation spectrum for molecule **C1** is recorded by collecting emission at 440 nm.

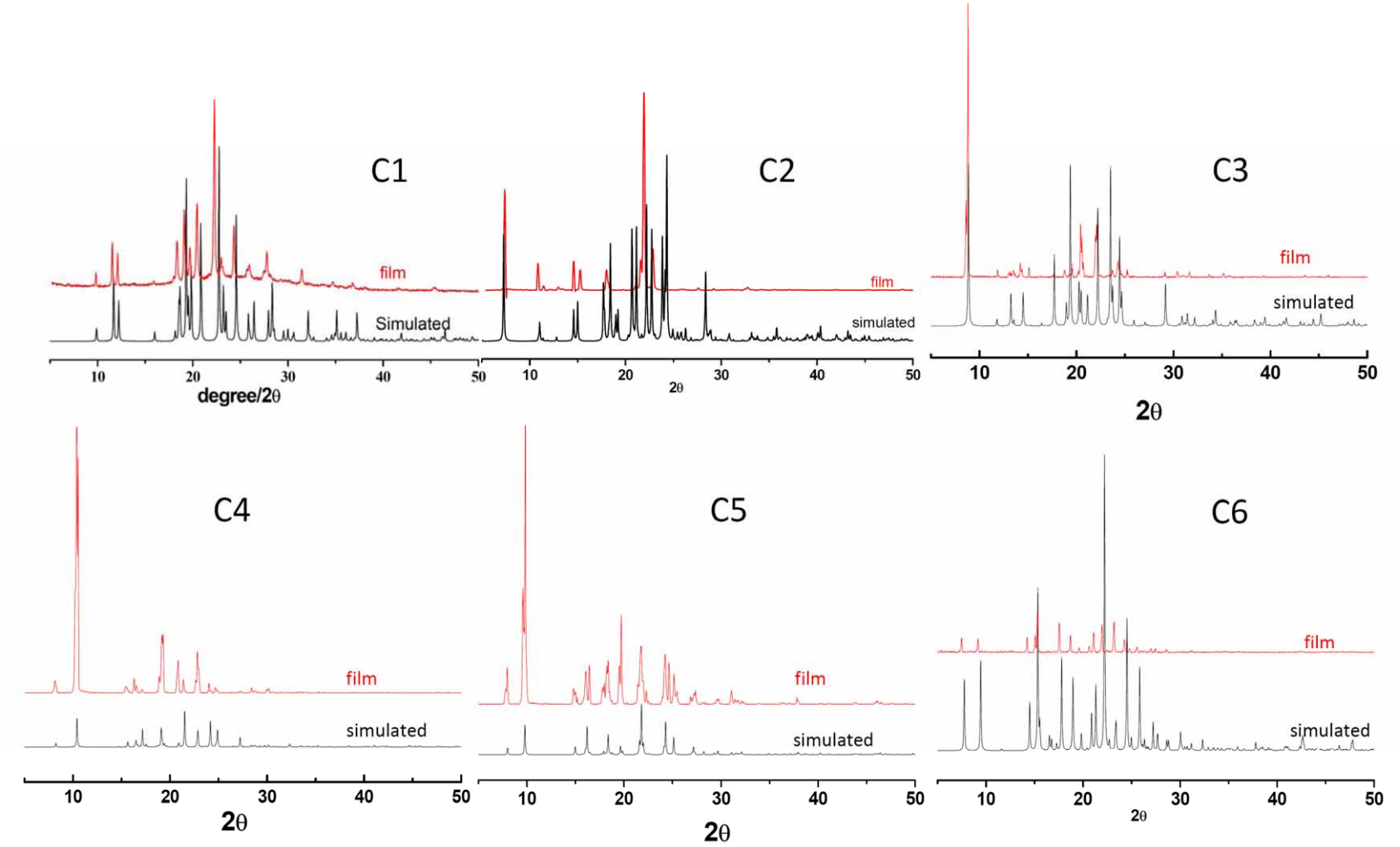

Figure S3: Comparison of XRD pattern recorded from the films of **C1** – **C6** used for fluorescence studies and that simulated from the single crystal X-ray diffraction data.

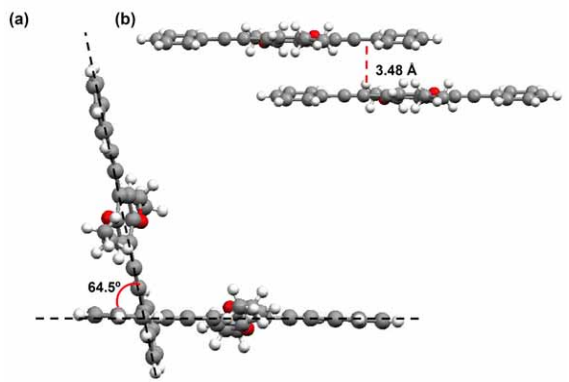

Figure S4: Intermolecular interaction possibility in molecule **C2** (a) a cross stacked pair of molecules and (b) a parallel slipped pair.

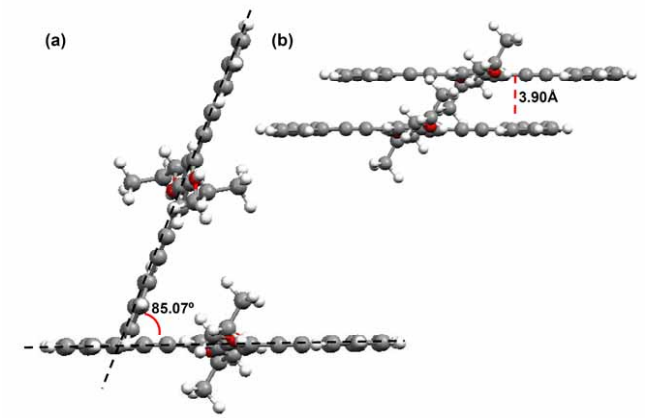

Figure S5: Intermolecular interaction possibility in molecule **C3** (a) cross stacked pair of molecules and (b) a parallel slipped pair.

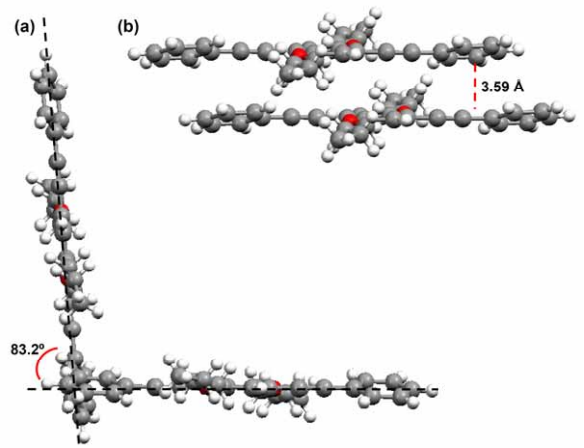

Figure S6: Intermolecular interaction possibility in molecule **C4** (a) cross stacked pair of molecules and (b) a parallel slipped pair.

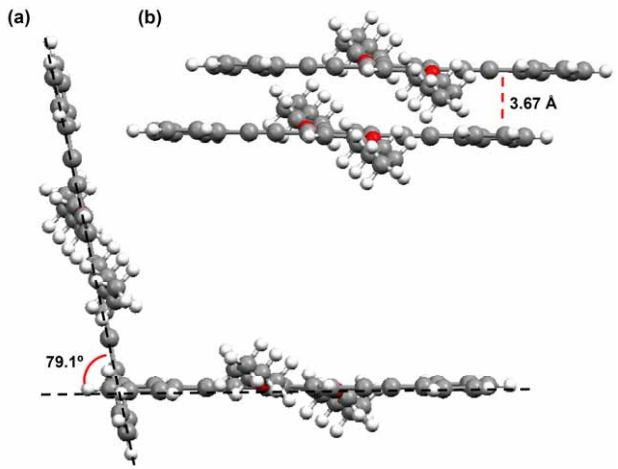

Figure S7: Intermolecular interaction possibility in molecule **C5** (a) cross stacked pair of molecules and (b) a parallel slipped pair.

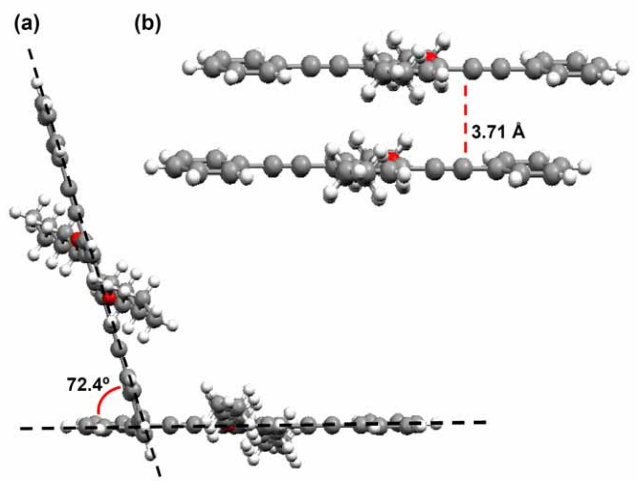

Figure S8: Intermolecular interaction possibility in molecule **C6** (a) cross stacked pair of molecules and (b) a parallel slipped pair.