An investigation on single crystal growth, structural, thermal and optical properties of a series of organic D–π–A push-pull materials

Vinod Kumar Gupta and Ram Adhar Singh*

Department of Chemistry, Centre of Advanced Study, Faculty of Science, Banaras Hindu University, Varanasi-221 005, INDIA

Email: **prrasingh@gmail.com**

Supporting Information

I. NMR spectra (^{1}H and ^{13}C)

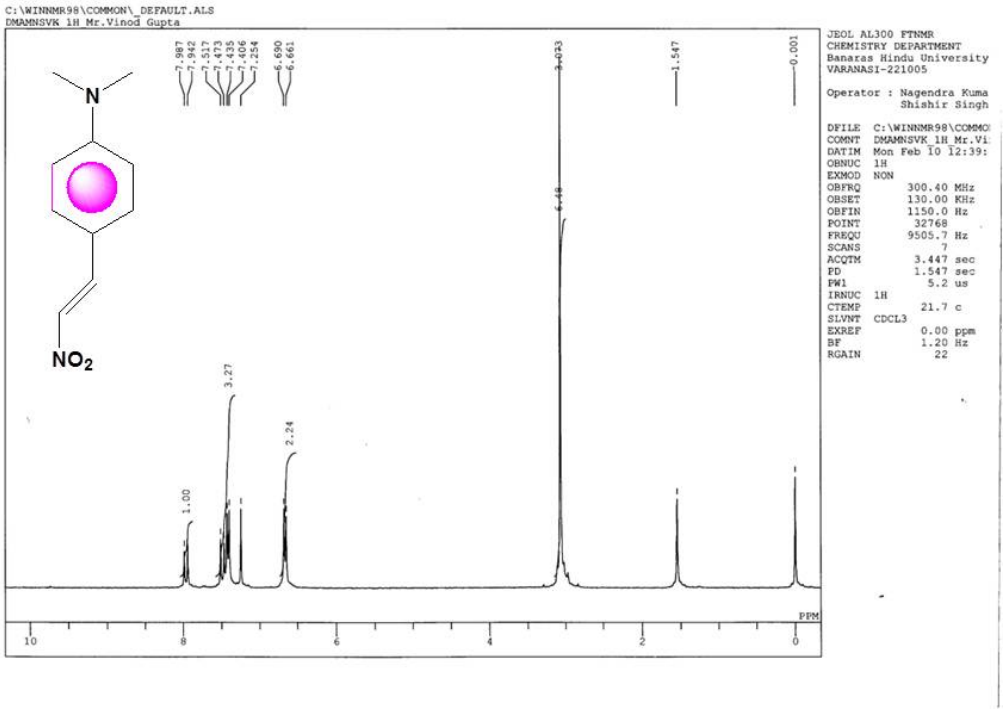

Fig. S1: ^{1}H NMR spectrum of chromophore **1**

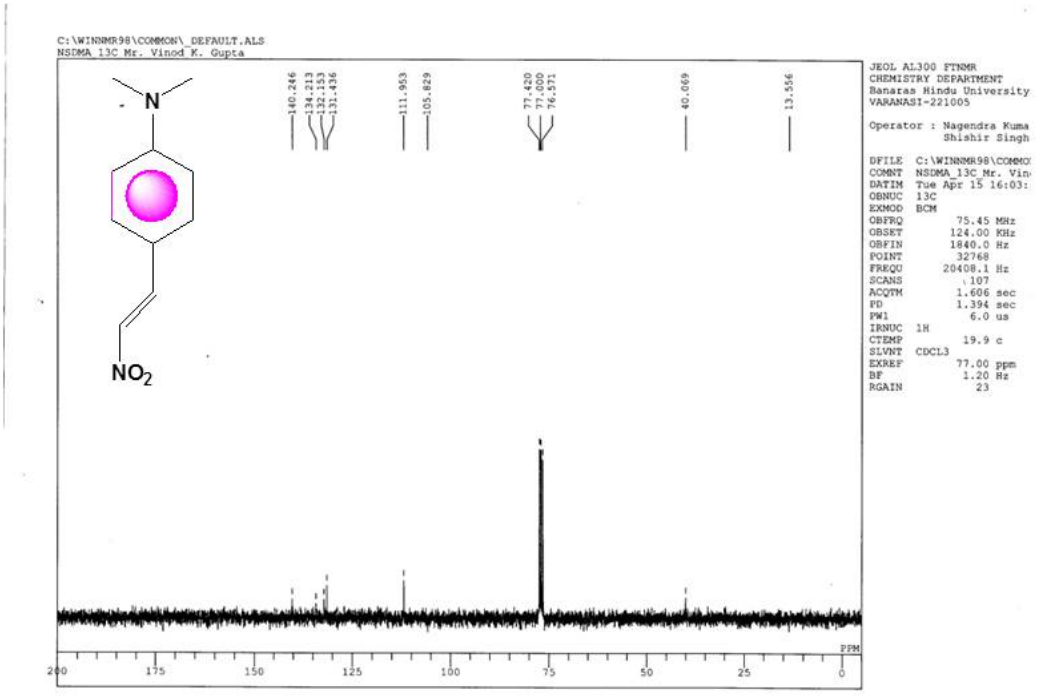

Fig. S2: ^{13}C NMR spectrum of chromophore **1**

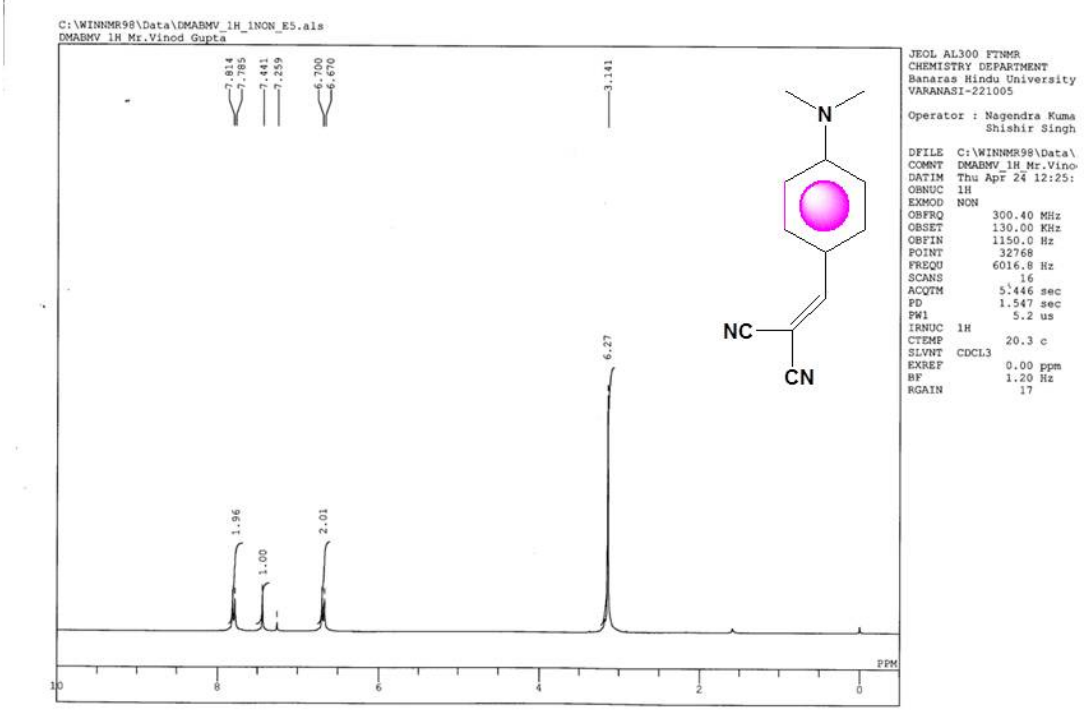

Fig. S3: ^{1}H NMR spectrum of chromophore **2**

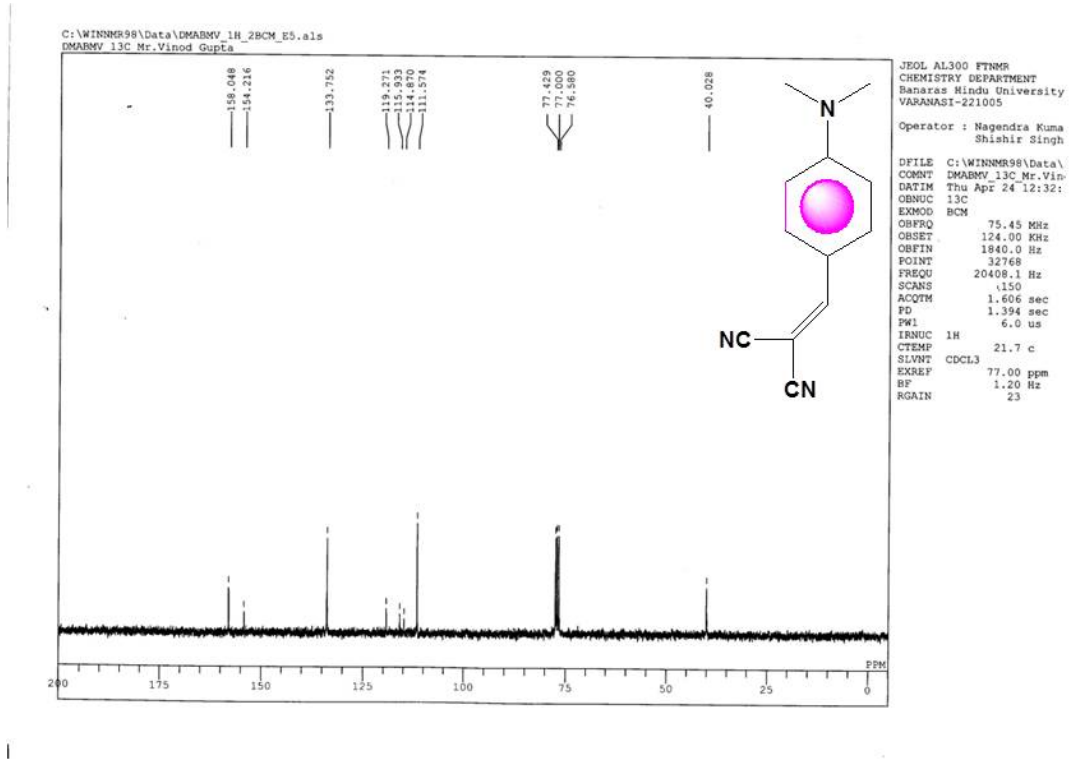

Fig. S4: ^{13}C NMR spectrum of chromophore **2**

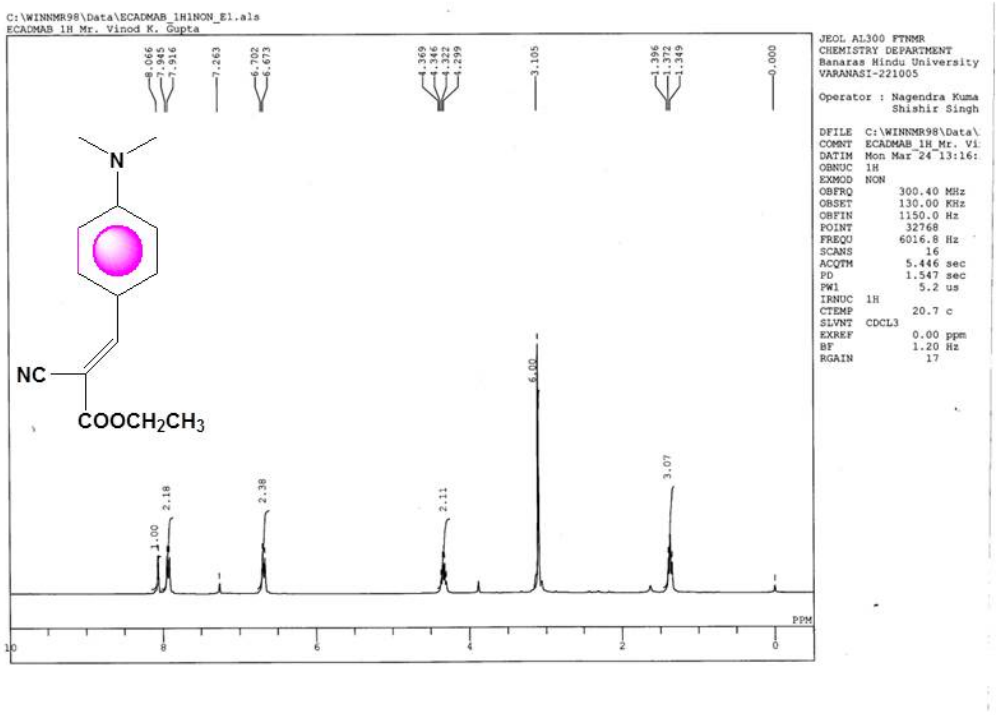

Fig. S5: ^{1}H NMR spectrum of chromophore **3**

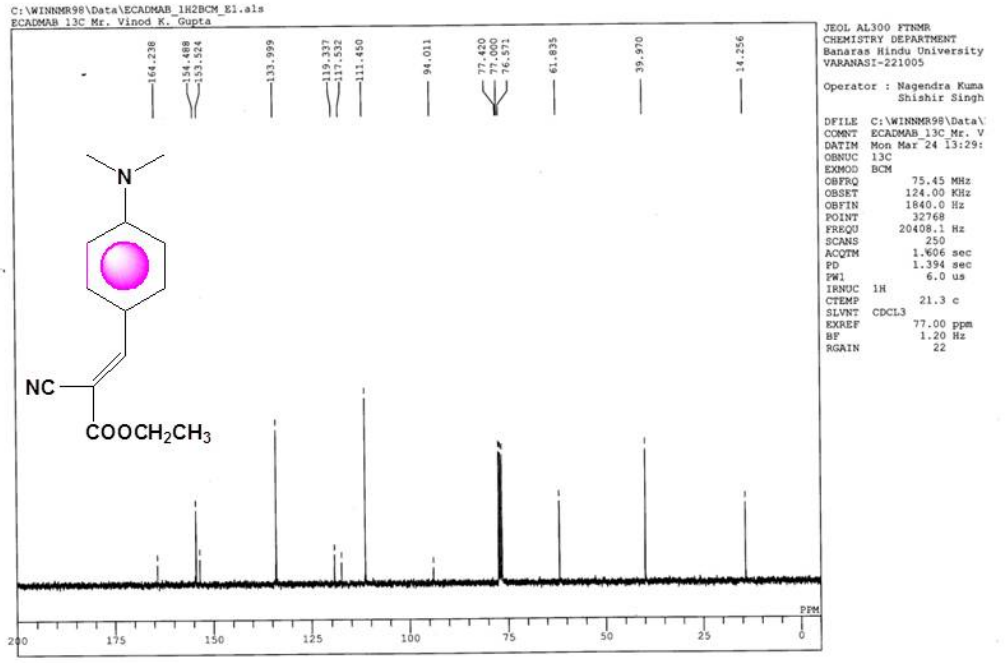

Fig. S6: ^{13}C NMR spectrum of chromophore **3**

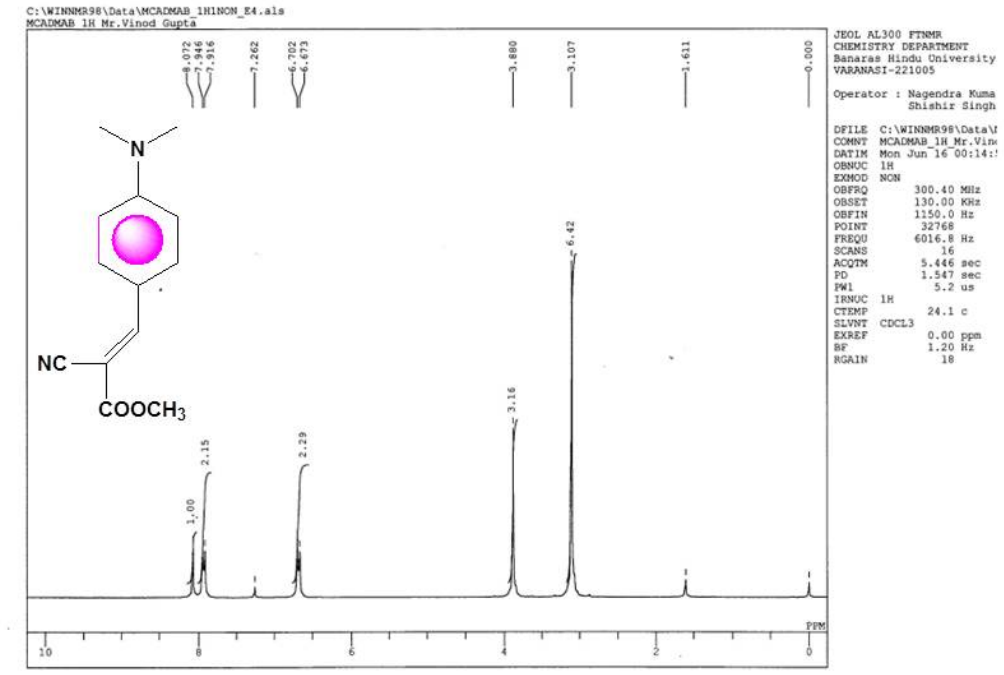

Fig. S7: ^{1}H NMR spectrum of chromophore **4**

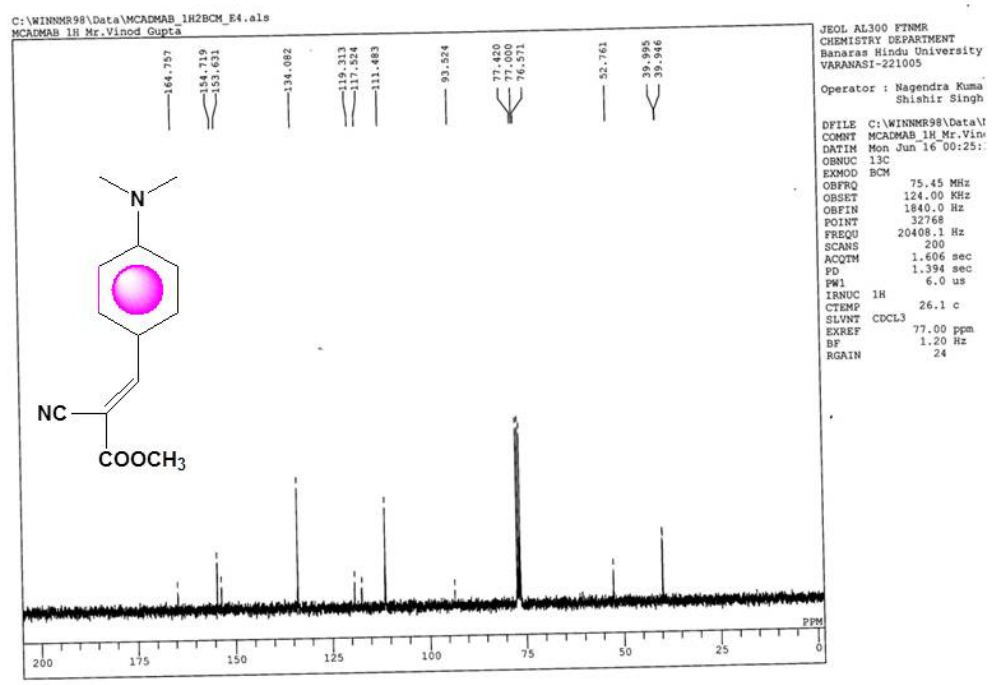

Fig. S8: ^{13}C NMR spectrum of chromophore **4**

II. Table S1: Solubility in 1:2 acetone-methanol mixture

Chromophore	Solubility (g/100 g of solvent)[a]
1	0.49
2	0.61
3	2.60
4	1.10

[a]Solubility at 28.0 ^{o}C in mixed 1:2 acetone-methanol (by weight) solvent.

III. Plots of 1/T versus lnN_s

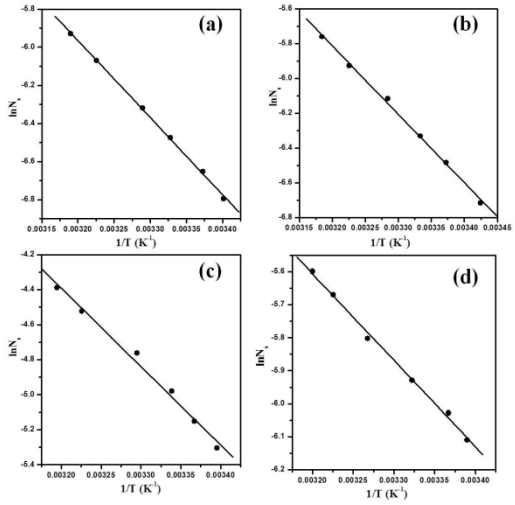

Fig. S9: Plot of 1/T versus lnN_s for (a) chromophore **1**, (b) chromophore **2**, (c) chromophore **3** and (d) chromophore **4** in 1:1 acetone-methanol mixed solvent.

IV. Crystal structure study and refinement

For single crystal X-ray diffraction studies, a suitable single crystal of all the chromophores with approximate dimensions were selected and mounted on a glass needle with the help of grease. The crystal's diffractions were recorded by using the Xcalibur oxford CCD diffractometer. The data reduction was carried out using Chrysalis Pro software. The structures were solved by direct method (SHELXL-97) and refined against all data by full matrix least-square on F^2using anisotropic displacement parameters for all non-hydrogen

atoms. All hydrogen atoms were included in the refinement at geometrically ideal positions and refined with a riding model.

V. Bond lengths and bond angles

Table S2: Bond Lengths (Å) and Bond Angles (deg) in the Structures Studied

Chromophore 1					
N(2)–C(6)	1.359(4)	N(2)–C(10)	1.450(4)	N(2)–C(9)	1.453(4)
C(6)–C(7)	1.407(4)	C(6)–C(5)	1.415(4)	C(3)–C(4)	1.375(4)
C(3)–C(8)	1.388(5)	C(3)–C(2)	1.503(6)	C(8)–C(7)	1.389(5)
C(8)–H(8)	0.9300	C(5)–C(4)	1.363(4)	C(5)–H(5)	0.9300
C(7)–H(7)	0.9300	C(4)–H(4)	0.9300	C(10)–H(10A)	0.9600
C(10)–H(10B)	0.9600	C(10)–H(10C)	0.9600	C(2)–C(1)	1.238(6)
C(2)–H(2)	0.9300	C(9)–H(9A)	0.9600	C(9)–H(9B)	0.9600
C(9)–H(9C)	0.9600	O(2)–N(1)	1.238(5)	N(1)–O(1)	1.220(5)
N(1)–C(1)	1.443(5)	C(1)–H(1)	0.9300		
C(6)–N(2)– C(10)	121.4(3)	C(6)–N2–C(9)	120.9(3)	C(10)–N(2)–C(9)	117.1(3)
N(2)–C(6)–C(7)	123.1(3)	N(2)–C(6)–C(5)	121.1(3)	C(7)–C(6)–C(5)	115.8(3)
C(4)–C(3)–C(8)	116.3(3)	C(4)–C(3)–C(2)	117.5(3)	C(8)–C(3)–C(2)	126.2(3)
C(3)–C(8)–C(7)	122.3(3)	C(3)–C(8)–H(8)	118.8	C(7)–C(8)–H(8)	118.8
C(4)–C(5)–C(6)	121.4(3)	C(4)–C(5)–H(5)	119.3	C(6)–C(5)–H(5)	119.3
C(8)–C(7)–C(6)	120.9(3)	C(8)–C(7)–H(7)	119.6	C(6)–C(7)–H(7)	119.6
C(5)–C(4)–C(3)	123.2(3)	C(5)–C(4)–H(4)	118.4	C(3)–C(4)–H(4)	118.4
N(2)–C(10)–H(10A)	109.5	N(2)–C(10)–H(10B)	109.5	H(10A)–C(10)–H(10B)	109.5
N(2)–C(10)–H(10C)	109.5	H(10A)–C(10)–H(10C)	109.5	H(10B)–C(10)–H(10C)	109.5
C(1)–C(2)–C(3)	126.7(5)	C(1)–C(2)–H(2)	116.7	C(3)–C(2)–H(2)	116.7
N(2)–C(9)–H(9A)	109.5	N(2)–C(9)–H(9B)	109.5	H9(A)–C(9)–H(9B)	109.5
N(2)–C(9)–H(9C)	109.5	H(9A)–C(9)–H(9C)	109.5	H(9B)–C(9)–H(9C)	109.5
O(1)–N(1)–O(2)	122.6(4)	O(1)–N(1)–C(1)	113.1(5)	O(2)–N(1)–C(1)	124.3(4)
C(2)–C(1)–N(1)	120.6(5	C(2)–C(1)–H(1)	119.7	N(1)–C(1)–H(1)	119.7
Chromophore 2					
N(1)–C(1)	1.352(4)	N(1)–C(11)	1.453(4)	N(1)–C(12)	1.455(4)
C(2)–C(3)	1.375(4)	C(2)–C(1)	1.395(4)	C(2)–H(2)	0.9300
C(4)–C(3)	1.386(4)	C(4)–C(5)	1.415(4)	C(4)–C(7)	1.422(4)
C(1)–C(6)	1.406(4)	C(6)–C(5)	1.373(3)	C(6)–H(6)	0.9300
C(5)–H(5)	0.9300	C(3)–H(3)	0.9300	C(8)–C(7)	1.367(4)
C(8)–C(9)	1.417(4)	C(8)–C(10)	1.430(4)	C(7)–H(7)	0.9300
C(11)–H(11B)	0.9600	C(11)–H(11C)	0.9600	C(11)–H(11A)	0.9600
C(12)–H(12B)	0.9600	C(12)–H(12C)	0.9600	C(12)–H(12A)	0.9600
N(3)–C(9)	1.143(4)	C(10)–N(2)	1.127(4)		
C(1)–N(1)–C(11)	122.3(3)	C(1)–N(1)–C(12)	121.3(3)	C(11)–N(1)–C(12)	116.4(3)
C(3)–C(2)–C(1)	120.4(4)	C(3)–C(2)–H(2)	119.8	C(1)–C(2)–H(2)	119.8
C(3)–C(4)–C(5)	116.3(3)	C(3)–C(4)–C(7)	118.7(3)	C(5)–C(4)–C(7)	125.0(3)
N(1)–C(1)–C(2)	121.2(3)	N(1)–C(1)–C(6)	121.1(3)	C(2)–C(1)–C(6)	117.6(3)
C(5)–C(6)–C(1)	121.2(3)	C(5)–C(6)–H(6)	119.4	C(1)–C(6)–H(6)	119.4
C(6)–C(5)–C(4)	121.4(3)	C(6)–C(5)–H(5)	119.3	C(4)–C(5)–H(5)	119.3
C(2)–C(3)–C(4)	123.1(3)	C(2)–C(3)–H(3)	118.5	C(4)–C(3)–H(3)	118.5
C(7)–C(8)–C(9)	119.3(3)	C(7)–C(8)–C(10)	125.6(3)	C(9)–C(8)–C(10)	114.9(4)
C(8)–C(7)–C(4)	132.0(3)	C(8)–C(7)–H(7)	114.0	C(4)–C(7)–H(7)	114.0
N(1)–C(11)–H(11B)	109.5	N(1)–C(11)–H(11C)	109.5	H(11B)–C(11)–H(11C)	109.5
N(1)–C(11)–H(11A)	109.5	H(11B)–C(11)–H(11A)	109.5	H(11C)–C(11)–H(11A)	109.5
N(1)–C(12)–H(12B)	109.5	N(1)–C(12)–H(12C)	109.5	H(12B)–C(12)–H(12C)	109.5
N(1)–C(12)–H(12A)	109.5	H(12B)–C(12)–H(12A)	109.5	H(12C)–C(12)–H(12A)	109.5
N(2)–C(10)–C(8)	177.7(5)	N(3)–C(9)–C(8)	178.0(4)		

Chromophore 3

N(2)–C(4)	1.3568(17)	N(2)–C(14)	1.442(2)	N(2)–C(13)	1.4564(19)
C(1)–C(6)	1.405(2)	C(1)–C(2)	1.4059(18)	C(1)–C(7)	1.4316(19)
C(7)–C(8)	1.3550(19)	C(7)–H(7)	0.9300	C(6)–C(5)	1.371(2)
C(6)–H(6)	0.9300	C(2)–C(3)	1.3630(19)	C(2)–H(2)	0.9300
C(5)–C(4)	1.4147(19)	C(5)–H(5)	0.9300	O(2)–C(10)	1.3418(18)
O(2)–C(11)	1.452(2)	C(8)–C(9)	1.429(2)	C(8)–C(10)	1.481(2)
C(10)–O(1)	1.1990(19)	C(3)–C(4)	1.409(2)	C(3)–H(3)	0.9300
C(14)–H(14)	0.9600	C(14)–H(14C)	0.9600	C(14)–H(14B)	0.9600
C(9)–N(1)	1.141(2)	C(13)–H(13A)	0.9600	C(13)–H(13C)	0.9600
C(13)–H(13B)	0.9600	C(11)–C(12)	1.466(3)	C(11)–H(11B)	0.9700
C(11)–H(11A)	0.9700	C(12)–H(12C)	0.9600	C(12)–H(12B)	0.960
C(12)–H(12A)	0.9600				
C(4)–N(2)–C(14)	121.07(12)	C(4)–N(2)–C(13)	120.95(13)	C(14)–N(2)–C(13)	117.42(13)
C(6)–C(1)–C(2)	115.95(12)	C(6)–C(1)–C(7)	126.39(12)	C(2)–C(1)–C(7)	117.67(13)
C(8)–C(7)–C(1)	132.63(15)	C(8)–C(7)–H(7)	113.7	C(1)–C(7)–H(7)	113.7
C(5)–C(6)–C(1)	122.04(13)	C(5)–C(6)–H(6)	119.0	C(1)–C(6)–H(6)	119.0
C(3)–C(2)–C(1)	122.80(13)	C(3)–C(2)–H(2)	118.6	C(1)–C(2)–H(2)	118.6
C(6)–C(5)–C(4)	121.45(13)	C(6)–C(5)–H(5)	119.3	C(4)–C(5)–H(5)	119.3
C(10)–O(2)–C(11)	117.12(15)	C(7)–C(8)–C(9)	123.62(14)	C(7)–C(8)–C(10)	118.60(14)
C(9)–C(8)–C(10)	117.78(13)	O(1)–C(10)–O(2)	123.94(15)	O(1)–C(10)–C(8)	124.21(14)
O(2)–C(10)–C(8)	111.85(14)	C(2)–C(3)–C(4)	121.19(13)	C(2)–C(3)–H(3)	119.4
C(4)–C(3)–H(3)	119.4	N(2)–C(14)–H(14)	109.5	N(2)–C(14)–H(14C)	109.5
H(14)–C(14)–H(14C)	109.5	N(2)–C(14)–H(14B)	109.5	H(14)–C(14)–H(14B)	109.5
H(14C)–C(14)–H(14B)	109.5	N(1)–C(9)–C(8)	179.70(17)	N(2)– C(13)–H(13A)	109.5
N(2)–C(13)–H(13C)	109.5	H(13A)–C(13)–H(13C)	109.5	N(2)–C(13)–H(13B)	109.5
H(13A)–C(13)–H(13B)	109.5	H(13C)–C(13)–H(13B)	109.5	O(2)–C(11)–C(12)	112.21(16)
O(2)–C(11)–H(11B)	109.2	C(12)–C(11)–H(11B)	109.2	O(2)–C(11)–H(11A)	109.2
C(12)–C(11)–H(11A)	109.2	H(11B)–C(11)–H(11A)	107.9	C(11)–C(12)–H(12C)	109.5
C(11)–C(12)–H(12B)	109.5	H(12C)–C(12)–H(12B)	109.5	C(11)–C(12)–H(12A)	109.5
H(12C)–C(12)–H(12A)	109.5	H(12B)–C(12)–H(12A)	109.5	N(2)–C(4)–C(3)	121.82(12)
N(2)–C(4)–C(5)	121.62(13)	C(3)–C(4)–C(5)	116.56(13)		

Chromophore 4

C(7)–C(8)	1.352(2)	C(7)–C(1)	1.438(2)	C(7)–H(7)	0.9300
O(2)–C(10)	1.343(2)	O(2)–C(11)	1.437(2)	N(1)–C(4)	1.361(2)
N(1)–C(13)	1.443(2)	N(1)–C(12)	1.445(2)	C(4)–C(5)	1.404(2)
C(4)–C(3)	1.410(2)	C(8)–C(9)	1.431(2)	C(8)–C(10)	1.473(2)
O(1)–C(10)	1.197(2)	C(9)–N(2)	1.145(2)	C(6)–C(5)	1.366(2)
C(6)–C(1)	1.396(2)	C(6)–H(6)	0.9300	C(1)–C(2)	1.399(2)
C(5)–H(5)	0.9300	C(2)–C(3)	1.362(2)	C(2)–H(2)	0.9300
C(3)–H(3)	0.9300	C(13)–H(13A)	0.9600	C(13)–H(13B)	0.9600
C(13)–H(13C)	0.9600	C(12)–H(12A)	0.9600	C(12)–H(12B)	0.9600
C(12)–H(12C)	0.9600	C(11)–H(11A)	0.9600	C(11)–H(11B)	0.9600
C(11)–H(11C)	0.9600				
C(8)–C(7)–C(1)	132.04(16)	C(8)–C(7)–H(7)	114.0	C(1)–C(7)–H(7)	114.0
C(10)–O(2)–C(11)	116.09(15)	C(4)–N(1)–C(13)	120.85(15)	C(4)–N(1)–C(12)	121.09(15)
C(13)–N(1)–C(12)	118.06(14)	N(1)–C(4)–C(5)	122.15(15)	N(1)–C(4)–C(3)	121.44(15)
C(5)–C(4)–C(3)	116.41(14)	C(7)–C(8)–C(9)	124.43(15)	C(7)–C(8)–C(10)	118.55(15)
C(9)–C(8)–C(10)	117.02(14)	N(2)–C(9)–C(8)	179.6(2)	C(5)–C(6)–C(1)	122.44(16)
C(5)–C(6)–H(6)	118.8	C(1)–C(6)–H(6)	118.8	C(6)–C(1)–C(2)	116.40(14)
C(6)–C(1)–C(7)	118.03(15)	C(2)–C(1)–C(7)	125.57(15)	C(6)–C(5)–C(4)	121.17(16)
C(6)–C(5)–H(5)	119.4	C(4)–C(5)–H(5)	119.4	C(3)–C(2)–C(1)	121.81(16)
C(3)–C(2)–H(2)	119.1	C(1)–C(2)–H(2)	119.1	O(1)–C(10)–O(2)	122.75(16)
O(1)–C(10)–C(8)	125.15(16)	O(2)–C(10)–C(8)	112.08(15)	C(2)–C(3)–C(4)	121.74(16)
C(2)–C(3)–H(3)	119.1	C(4)–C(3)–H(3)	119.1	N(1)–C(13)–H(13A)	109.5
N(1)–C(13)–H(13B)	109.5	H(13A)–C(13)–H(13B)	109.5	N(1)–C(13)–H(13C)	109.5
H(13A)–C(13)–H(13C)	109.5	H(13B)–C(13)–H(13C)	109.5	N(1)–C(12)–H(12A)	109.5
N(1)–C(12)–H(12B)	109.5	H(12A)–C(12)–H(12B)	109.5	N(1)–C(12)–H(12C)	109.5
H(12A)–C(12)–H(12C)	109.5	H(12B)–C(12)–H(12C)	109.5	O(2)–C(11)–H(11A)	109.5
O(2)–C(11)–H(11B)	109.5	H(11A)–C(11)–H(11B)	109.5	O(2)–C(11)–H(11C)	109.5
H(11A)–C(11)–H(11C)	109.5	H(11B)–C(11)–H(11C)	109.5		

VI. View of C–H...π interactions

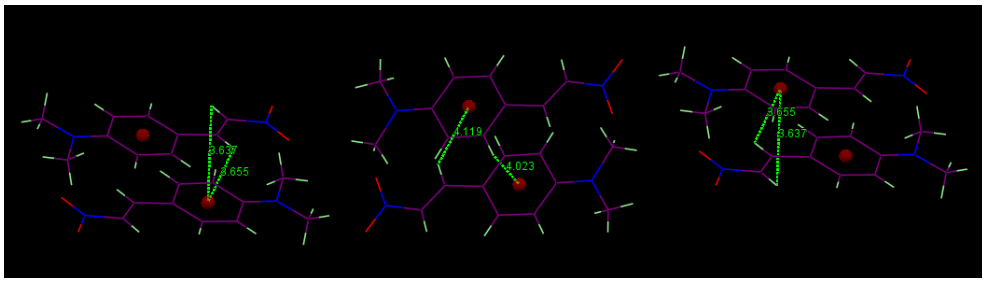

Fig. S10: View of C–H...π interactions in chromophore **1**

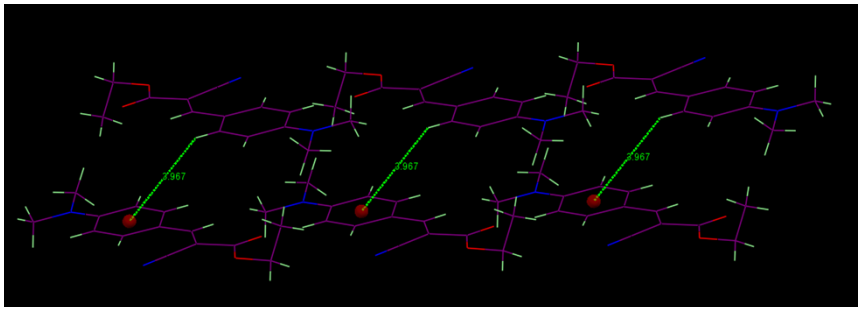

Fig. S11: View of C–H...π interactions in chromophore **3**

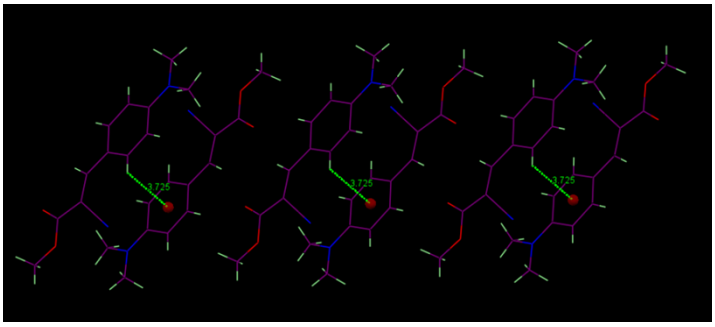

Fig. S12: View of C–H...π interactions in chromophore **4**

VII. Orientation of molecules in unit cell

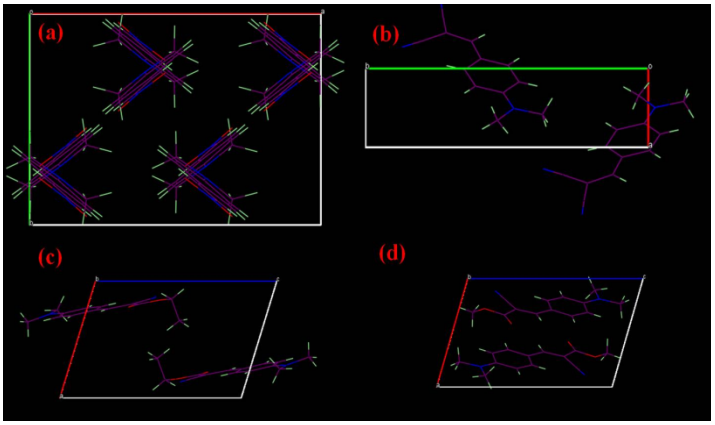

Fig. S13: Orientation of chromophores (a) **1**, (b) **2**, (c) **3** and (d) **4** in unit cell.

VIII. Thermal activation energy plots

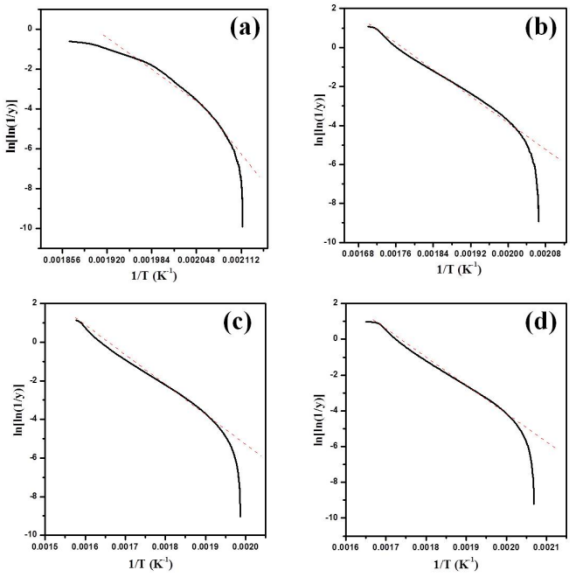

Fig. S14: Thermal activation energy plots of (a) chromophore **1**, (b) chromophore **2, (c)** chromophore **3** and (d) chromophore **4.**

IX. UV-Vis. absorption spectra in different solvents

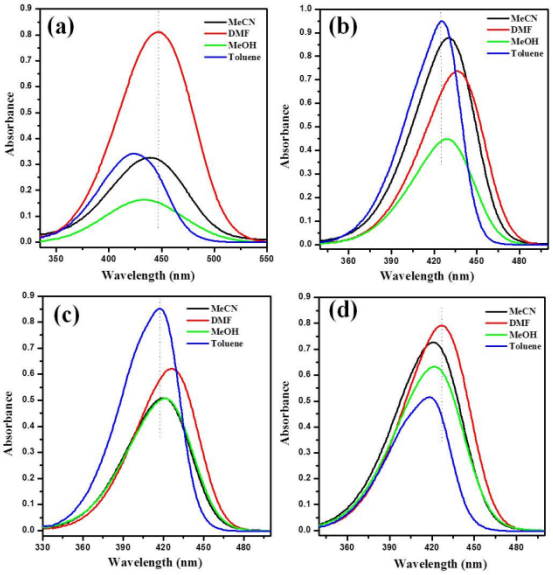

Fig. S15: Absorption spectra of (a) chromophore **1**, (b) chromophore **2**, (c) chromophore **3** and (d) chromophore **4**; in different solvents with molar concentration 1.0×10^{-5} M.

X. Fluorescence spectra in different solvents

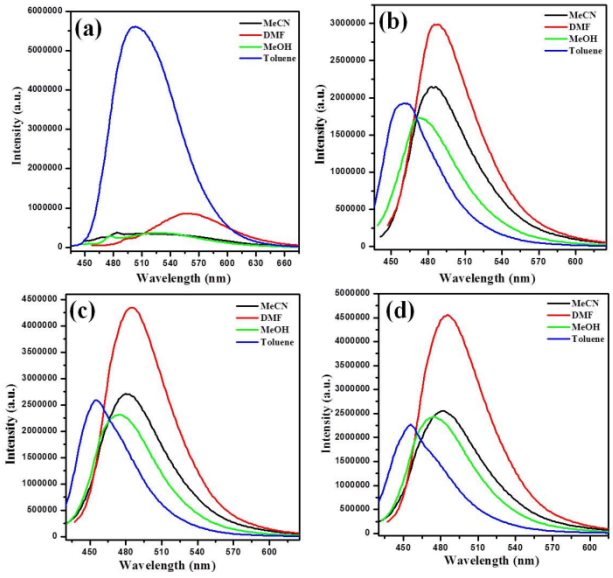

Fig. S16: Fluorescence spectra of (a) chromophore **1**, (b) chromophore **2**, (c) chromophore **3** and (d) chromophore **4**; in different solvents with molar concentration 1.0×10^{-5} M.

XI. Lippert-Mataga plots

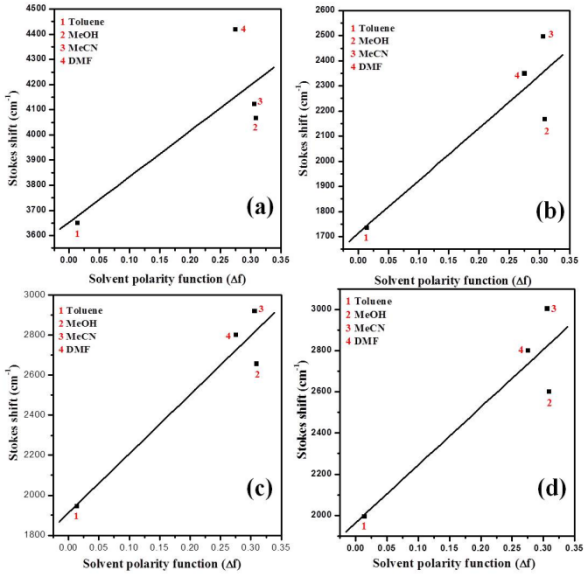

Fig. S17: Lippert-Mataga plots of Stokes shift against the solvent polarity function (Δf) for (a) chromophore **1**, (b) chromophore **2, (c)** chromophore **3** and (d) chromophore **4**.