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Supporting Information

A low molecular weight OLED material:2-(4-((2-hydroxyethyl)(methyl) amino)-benzylidene)malononitrile. Synthesis, crystal structure, thin film morphology, spectroscopic characterization and DFT calculations

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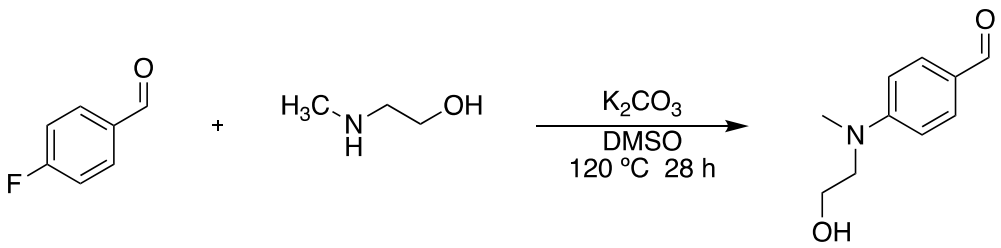
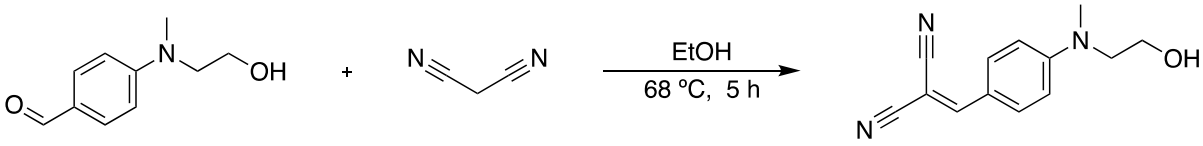
Synthesis of 4-((2-hydroxyethyl)(methyl)amino)benzaldehyde [HEMAB]



A mixture of 4-Fluorobenzaldehyde (500mg, 0.39mmol), *N*-methylethanolamine (600mg, 0.80mmol) and K_2CO_3 (550mg, 0.40 mmol) was taken in DMSO (2 mL) and refluxed at 120 °C for 28 hours with constant stirring. The completion of the reaction was monitored by color change from transparent to light-yellow until to be dark orange. After the completion of the reaction, the crude production was cooled to rt, added water to it (50 mL). The crude product was extracted with ethyl acetate (2 x 20 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and the evaporate the solvent. The precipitate was formed in a greater quantity and washed by cold EtOH (4 °C) until a yellow powder was obtained. The yellow powder was purified with a Hex:EtOAc mixture (3:1). The expected product yield obtained 96% as a yellow powder. M.p. 66-68 °C.

FT-IR (KBr), $\tilde{\nu}$(cm^{-1}) 3399 (νO-H) (m), 2928 ($\nu_{as}C\text{-}H_{CH2}$) (m), 2874 ($\nu_{s}C\text{-}H_{CH3}$) (m), 2838 (νC-H, $_{CHO}$)(w), 1642 (νC=O, $_{-CHO}$) (s), 1433 ($\delta_{s}C\text{-}H_{CH2}$) (w), 1394 ($\delta_{as}C\text{-}H_{CH3}$)(m), 1313,1246, 1207 (νC-N) (m), 1170 (νC-C, Ar) (s) , 1054 (νC-O_{OH}) (m), 722 (p-C-H_{CH2}) (w). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm), δ 3.14 (s, 3H-CH_3), 3.64 (t, *J* = 5, 5 Hz, 2H, -CH_2), 3.89 (t, *J* = 5, 10, 7.5 Hz, 2H, CH_2H), 6.78 (d, *J* = 10 Hz, 2H, Ar), 7.72 (d, *J* = 5 Hz, 2H, -Ar), 9.71 (s, 1H, -CHO). **^{13}C NMR** (125 MHz, $CDCl_3$, ppm), δ 39.25 (-CH_3), 54.36 (-CH_2), 60.07 (-CH_2), 111.17 (-Ar), 125.29 (-Ar), 132.18 (-ipso), 153.90 (ipso), 190.47 (CO). **MS,** m/z (Ir/%): 179 (62), 148 (100) (M^+), 132 (47), 119 (20.5), 77 (27.4).

Synthesis of 2-(4-((2-hydroxyethyl)(methyl)amino)benzylidene)malononitrile). [HEMABM]



To ethanolic solution of **HEMAB** (0.201g in 3.8 mL ethanol, 1.11 mmol) was taken in the 25 mL two-neck round-bolted flask. The slowly add the ethanolic solution of malononitrile

(75 mg in 1.2 mL ethanol, 1.11 mmol) with constant stirring. Then reaction mixture was stirred for 5 hours at 68 °C. During the reaction period, the color of reaction was changed from orange, red to dark brown. After that the reaction mixture was concentrated to get viscous dark brown liquid, and it was washed with cyclohexane (2 mL) to get precipitate the product. The precipitate was filtered under vacuum and dried. Finally, the dark powder was recrystallized in toluene (12 mL), and washed with hexane (2 mL) to obtain an orange solid, the product was obtained in 69 % yield and with a m.p. of 102-104 °C.

HEMABM. FT-IR KBr (ν/cm^{-1}): 3480 (νO-H), 2940 (νC-H), 2216 (νC≡N), 1608 ($\nu R_1R_2C=CHR_3$), 1566, 1522 ($C=C_a$), 1261, 1195 ($C-N_t$), 1047 ($\nu C-O_{OH}$), 823 (δC-H). 500MHz, H^1-NMR ($CDCl_3$ ppm): 7.83 (2H, d, *J* =10Hz, ArH), 7.48 (1H, s,=CH), 6.78 (2H, d, *J* =10Hz, ArH), 3.93-3.90 (2H, q, *J* =5 Hz, $-CH_2$), 3.68 (2H, t, *J* = 10Hz, $-CH_2$), 3.20 (3H, s, $-NCH_3$), 2.20 (1H, s, -OH). MS, m/z (Ir/%): $[C_{13}H_{13}N_3O]$ 227, $[C_{13}H_{12}N_3O^{\bullet}]$ 226 $[C_9H_{12}NO^{\bullet}]$ 150, $[C_4HN_2^{\bullet}]$77.

The adequate crystals for **SCXRD** were obtained by slow evaporation, 20-50 mg of [**HEMABM**] was dissolved in 5.0 mL of $CHCl_3$, the solution was kept at 4 °C for 3 days until the appeared the single crystals orange color. Also, similar single crystals were obtained from the methanolic solution.

Table S1. Crystal data and refinement parameters for **HEMABM**

Parameters	**HEMABM**
Empirical formula	$C_{13}H_{13}N_3O$
Color, habit	orange, lath
Formula weight	227.26
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	110
a, *b*, *c* (Å)	7.24645 (14), 17.8507 (4), 9.27013 (18)
β (°)	92.1370 (16)
V (Å^3)	1198.30 (4)
Z	4
Dc(g cm^{-3})	
Radiation type	Cu *K*α
μ(mm^{-1})	0.67
Crystal size (mm)	0.34 × 0.09 × 0.04
T_{min}, T_{max}	0.857, 0.978
No. of measured, independent and observed [$I > 2\sigma I$)] reflections	7864, 2347, 1994
R_{int}	0.023
(sin θ_{max} (Å^{-1})	0.616
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.034, 0.094, 1.02
No. of reflections	2347
No. of parameters	307
No. of restraints	728
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.18, -0.13

Table S2. Bond lengths (Å) for **HEMABM**

Bond	Length (Å)
N(1)-C(1)	1.138(7)
c(1)-C(3)	1.418(6)
N(2)-C(2)	1.156(7)
C(2)-C(3)	1.430(6)
C(3)-C(4)	1.373(6)
C(4)-C(5)	1.430(7)
C(5)-C(6)	1.414(7)
C(5)-C(10)	1.418(7)
C(6)-C(7)	1.371(7)
C(7)-C(8)	1.415(4)
C(8)-N(3)	1.402(6)
C(8)-C(9)	1.423(6)
C(9)-C(10)	1.372(7)
N(3)-C(11)	1.455(6)
N(3)-C(12)	1.458(6)
C(12)-C(13)	1.529(5)
C(13)-O(1)	1.430(5)
O(1)-H(1)	0.8400
N(1')-C(1')	1.161(11)
C(1)-C(3')	1.429(10)
N(2')-C(2')	1.136(10)
C(2)-C(3')	1.440(10)
C(3')-C(4')	1.346(10)
C(4')-C(5')	1.424(10)
C(5')-C(10')	1.398(11)
C(5')-C(6')	1.399(11)
C(6')-C(7')	1.381(10)
C(13)-C(14)	1.399(7)
C(8')-C(9')	1.382(9)
C(8')-N(3')	1.478(11)
C(9')-C(10')	1.371(10)
N(3')-C(12')	1.455(9)
N(3')-C(11')	1.474(10)
C(12')-C(13')	1.517(6)
C(13')-O(1')	1.425(6)
O(1)-H(1')	0.8400
N(3C)-C(12C)	1.454(11)
N(3C)-C(11C)	1.457(12)
C(12C)-C(13C)	1.518(12)
C(13C)-O(1C)	1.415(13)
O(1C)-H(1C)	0.8400

Table S3. Torsion angles (º) for **HEMABM**

Bond	Angles(º)
C(2)-C(3)-C(4)-C(5)	179.7(16)
C(3)-C(4)-C(4)-C(6)	2(3)
C(3)-C(4)-C(5)-C(10)	-177.6(16)
C(10)-C(5)-C(6)-C(7)	-1(2)
C(4)-C(5)-C(6)-C(7)	179.8(15)
C(5)-C(6)-C(7)-C(8)	0.2(17)
C(6)-C(7)-C(8)-N(3)	-178.1(9)
C(6)-C(7)-C(8)-C(9)	0.5(11)
N(3)-C(8)-C(9)-C(10)	178.4(7)
C(7)-C(8)-C(9)-C(10)	-0.4(10)
C(8)-C(9)-C(10)-C(5)	-0.5(14)
C(6)-C(5)-C(10)-C(9)	1(2)
C(4)-C(5)-C(10)-C(9)	-179.6(13)
C(7)-C(8)-N(3)-C(11)	173.0(7)
C(9)-C(8)-N(3)-C(11)	-5.7(9)
C(7)-C(8)-N(3)-C(12)	-7.7(10)
C(9)-C(8)-N(3)-C(12)	173.7(6)
C(8)-N(3)-C(12)-C(13)	82.9(6)
C(11)-N(3)-C(12)-C(13)	-97.7(6)
N(3)-C(12)-C(13)-O(1)	56.8(7)
C(1')-C(3')-C(4')-C(5')	-1(4)
C(2')-C(3')-C(4')-C(5')	-177(3)
C(3')-C(4')-C(5')-C(10')	175(3)
C(3')-C(4')-C(5')-C(6')	-6(5)
C(10')-C(5')-C(6')-C(7')	2(3)
C(4')-C(5')-C(6')-C(7')	-178(2)
C(5')-C(6')-C(7')-C(8')	-1(3)
C(6')-C(7')-C(8')-C(9')	-1.6(18)
C(6')-C(7')-c(8')-N(3')	173.9(14)
C(7')-C(8')-C(9')-C(10')	3.4(17)
N(3')-C(8')-C(9')-C(10')	-168.4(17)
C(8')-C(9')-C(10')-C(5')	-3(2)
C(6')-C(5')-C(10')-C(9')	0(3)
C(4')-C(5')-C(10')-C(9')	-180(2)
C(9')-C(8')-N(3')-C(12')	-4(2)
C(7')-C(8')-N(3')-C(12')	-176.7(8)
C(9')-C(8')-N(3')-C(11')	-170.9(15)
C(7')-C(8')-N(3')-C(11')	16.5(17)
C(11')-N(3')-C(12')-C(13')	94.5(10)
C(8')-N(3')-C(12')-C(13')	-75.4(10)
N(3')-C(12')-C(13')-O(1')	-57.7(8)
C(11')-N(3C)-C(12C)-C(13C)	-97.8(14)
N(3C)-C(12C)-C(13C)-O(1C)	59.1(15)

All torsion angles follow the convention defined by Allen & Rogers (Allen, F.H. & Rogers, D. (1969) *Acta Cryst*. **B25**, 1326-1330)

Table S4. Optoelectronic properties for **HEMABM**

Oxidation Potential (eV)	1.5999
Reduction Potential (eV)	-1.3213
Hole Reorganization Energy (eV)	0.4150
Electron Reorganization Energy (eV)	0.5783
Triplet Energy (eV)	2.1130
Lmax (nm)	390
Emax (nm)	735
Stokes Shift	345
Triplet Stabilization Energy (eV)	0.2896
Hole Extraction Potential (eV)	7.0036
Electron Extraction Potential (eV)	-1.1959
Scaled HOMO (eV)	-6.1299
Scaled LUMO (eV)	-3.2087
Electron Small Polaron Stabilization Energy (eV)	0.3222
Hole Small Polaron Stabilization Energy (eV)	0.2766
Triplet Reorganization Energy (eV)	0.5661
T1 Vertical Emission (eV)	1.8223
T1 Vertical Absorption (eV)	2.3884
T1 Raw Triplet Energy (eV)	2.0988
S1-T1 Gap (eV)	1.4291
S1-T2 Gap (eV)	0.1397
S1-T3 Gap (eV)	-0.2758
Dipole (D)	9.3701

Table S5. Second order perturbation theory analysis of Fock matrix in NBO basis for **HEMABM**

Donor(i)	**Type**	**Acceptor NBO (j)**	**Type**	**E2 (kcal mol^{-1})**
LP (1) N2	Lone pair	BD*(1) O1 – H1(O)	σ*	6.00
LP (1) C8	Lone pair	BD*(2) C3 - C4	π *	0.74
BD (1) O1 – H1(O)	σ	BD*(1) N2 – C2	π *	0.33