Supporting Information

Rational Design of Phenothiazine (PTz) and Ethylenedioxythiophene (EDOT) Based Donor-Acceptor Compounds with a Molecular Aggregation Breaker for Solid State Emission in Red and NIR region

Elumalai Ramachandran and Raghavachari Dhamodharan *

DEPARTMENT OF CHEMISTRY, INDIAN INSTITUTE OF TECHNOLOGY MADRAS, CHENNAI 600 036, TAMILNADU, INDIA.

E-mail: damo@iitm.ac.in
Scheme S1. Synthesis intermediates.

Scheme S1.

References:

Figure S1. $^1$H and $^{13}$C NMR spectra of 1

Expansion of $^{13}$C NMR spectrum of 1
Figure S2. $^1$H and $^{13}$C NMR spectra of 2
Expansion of $^{13}$C NMR spectrum of 2

[Diagram of NMR spectrum showing various chemical shifts and peak assignments]
DEPT NMR spectra of compounds 1 and 2:

**Figure S3.** DEPT spectrum of compound 1

**Figure S4.** DEPT NMR spectrum of compound 2
Figure S5. HMBC and HSQC NMR spectra of compound 1
Figure S6. HMBC and HSQC NMR spectra of compound 2
MALDI Spectra of compounds 1 and 2:

**Figure S7.** MALDI mass spectrum of compound 1

**Figure S8.** MALDI mass spectrum of compound 2
Data of X-ray crystallographic analysis of compound 1:

CCDC–921593 contains the supplementary crystallographic data for 1. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Empirical formula                 C_{46}H_{49}NO_{6}S_{3} 
Formula weight                 808.04 
Temperature                     298(2) K 
Wavelength                     0.71073 Å 
Crystal system                Triclinic 
Space group                    P-1 
Unit cell dimensions
\[ a = 5.3262(3) \text{ Å} \quad \alpha = 100.032(3)^\circ \]
\[ b = 13.1770(9) \text{ Å} \quad \beta = 92.318(2)^\circ \]
\[ c = 34.470(2) \text{ Å} \quad \gamma = 95.724(3)^\circ \]
Volume                           2366.2(3) Å³ 
Z                                 2 
Calculated density             1.134 g/cm³ 
Absorption coefficient              0.200 mm⁻¹ 
F(000)                          856 
Crystal size                     0.25 x 0.20 x 0.15 mm³ 
Theta range for data collection   0.60 to 25.00° 
Limiting indices                -6<=h<=5, -15<=k<=15, -40<=l<=40 
Reflections collected           21926 
Independent reflections       7690 [R(int) = 0.0408] 
Completeness to theta = 25.00       92.0 % 
Absorption correction              None 
Max. and min. transmission    0.9706 and 0.9516 
Refinement method               Full-matrix least-squares on F² 
Data / restraints / parameters     7690 / 0 / 506 
Goodness-of-fit on F²            1.062 
Final R indices [l>2sigma(I)]    R1 = 0.0793, wR2 = 0.2482 
R indices (all data)             R1 = 0.1416, wR2 = 0.2921 
Largest diff. peak and hole     0.743 and -0.322 e.A⁻³
Comparison of powder XRD of 1 in various forms:

**Figure S9.** Powder XRD pattern of compound 1 in crystal (red line), powder (blue line) and thin film form (violet) compared with the simulated data obtained from SXRD

Powder XRD pattern of the compounds 1 and 2:

**Figure S10.** Powder XRD Pattern of compounds 1 and 2
$^1$H NMR analysis of Acetone included crystals of 1

**Figure S11.** $^1$H NMR spectrum of 1 as crystallized (acetone at 2.1 ppm)

**Figure S12.** $^1$H NMR spectrum of 1 after heating at 70 °C for 10 minutes (amount of acetone at 2.1 ppm is reduced)
Figure S13. $^1$H NMR spectrum of 1 after heating at 70 °C for 20 minutes (amount of acetone at 2.1 ppm is reduced further)

Figure S14. $^1$H NMR spectrum of 1 after grinding well (acetone peak at 2.1 ppm is reduced even further)
Figure S15. $^1$H NMR spectrum of 1 after grinding well and heating for 30 minutes (acetone at 2.1 ppm is nearly disappeared)

Figure S16. IR spectrum of compound 1 as crystallized
**Figure S17.** IR spectrum of compound 1 slightly ground.

**Figure S18.** IR spectrum of compound 1 slightly ground with KBr.
Figure S19. IR spectrum of compound 1 strongly ground with KBr

Figure S20. IR spectrum of compound 1 strongly ground with KBr and heated for 30 minutes
Differential scanning calorimetry analysis of acetone included crystals of 1:

**Figure S21.** Differential scanning calorimetry traces of compounds 1 in single crystal form in the first cycle of heating at 1 °C / min followed by cooling at 1 °C / min and second cycle of heating and cooling at 1 °C / min.

**Figure S22.** Differential scanning calorimetry traces of compounds 1 in the as synthesized form in the first cycle of heating at 1 °C / min followed by cooling at 1 °C / min and second cycle of heating and cooling at 1 °C / min.
Thermogravimetric analysis (TGA) traces of compounds 1 and 2:

![Thermogravimetric analysis traces of compounds 1 and 2](image)

**Figure S23.** Thermogravimetric analysis traces of compounds 1 and 2

**Table S1.** Thermal properties of 1 and 2.

<table>
<thead>
<tr>
<th>Cmpd</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_p[^{o}C][^a]$</td>
<td>128</td>
<td>100</td>
</tr>
<tr>
<td>$T_d[^{o}C][^b]$</td>
<td>383</td>
<td>394</td>
</tr>
</tbody>
</table>

[^a]: determined using a melting point apparatus.  
[^b]: $T_d$: decomposition temperature at which the compound loses 5% of the weight as determined by TGA at a heating rate of 5 °C / min.
UV-visible absorption and fluorescence measurement of 1 and 2 in thin film form dispersed in polystyrene (PS) matrix

**Figure S24.** UV-visible and fluorescence spectra of aldehyde 1 (left) and dicyanovinyl compound 2 (right) in thin film form dispersed in PS matrix.

**Preparation of doped polystyrene (PS) films:**
The sample was dissolved in a saturated PS benzene solution (0.1 mg/mL). The resulting solution was dropped onto a quartz plate (10 mm × 10 mm) and spin-coated at 1000 rpm for 30 seconds. The PS film was dried under reduced pressure at 50 °C for 1 h.

**Figure S25.** 1 and 2 a) in toluene (left vial, 1; right vial, 2). b) as powder. c) drop cast film. d) doped in PS film (Top row, 1; bottom row, 2)

**CV Measurement:** Cyclic voltammetry (CV) was performed on a CHI 660D electrochemical analyzer. The CV cell consisted of Glassy carbon working electrode, Pt wire counter electrode, and Ag/AgCl reference electrode. A DCM solution of a sample with a concentration of 1 mM and 0.1 M tetrabutylammonium hexafluorophosphate (Bu4PF6) as supporting electrolyte were used for the measurement at a scan rate of 50 mV/s. The solvent (DCM) was degassed with nitrogen for 15 minutes before making the solution of the compound prior to each experiment.
Table S2. Computational data of compounds 1 and 2

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>500 (abs edge)</td>
<td>2.48</td>
<td>473</td>
<td>2.62</td>
<td>214→215 (0.69889) [HOMO → LUMO]</td>
<td>0.9487</td>
</tr>
<tr>
<td></td>
<td>419 (abs maximum)</td>
<td>2.95</td>
<td>368</td>
<td>3.36</td>
<td>213→216 (0.68591) [HOMO-1 → LUMO+1]</td>
<td>0.7640</td>
</tr>
<tr>
<td>2</td>
<td>584 (abs edge)</td>
<td>2.12</td>
<td>568</td>
<td>2.18</td>
<td>238→239 (0.70124) [HOMO → LUMO]</td>
<td>1.1880</td>
</tr>
<tr>
<td></td>
<td>493 (abs maximum)</td>
<td>2.51</td>
<td>438</td>
<td>2.83</td>
<td>237→240 (0.66884) [HOMO-1 → LUMO+1]</td>
<td>0.7494</td>
</tr>
</tbody>
</table>