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Structure – property correlations on nonlinear optical properties of a few bipodal D-π-A molecules - Experimental and theoretical approach

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This Supporting Information includes:

1 Experimental methods

Infrared spectra (FTIR) were recorded on JASCO 4100 model FTIR spectrometer. The ^{1}H NMR spectra were recorded on 400 MHz on Bruker FT-NMR spectrometer with tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in parts per million (ppm) downfield to tetramethylsilane.

1.2 Synthesis

All the molecules were synthesized based on methods reported in the literature[31,43,44] i.e., a mixture of appropriate aldehyde (10 mmol) with the active methylene compound PBA or PTBA (4 mmol), piperidine (0.5 ml), and toluene (20 ml) were refluxed under N_2 atmosphere for 48 h. The reaction mixture was allowed to cool to room temperature, poured into distilled water and extracted with chloroform. The organic extracts were washed several times with distilled water, dried over anhydrous sodium sulphate and the solvent was removed under vacuum. The residue obtained was subjected to column chromatography 60-120 mesh silica gel with ethyl acetate: petroleum ether (3:1) as the eluent. All the synthesized molecules were characterized by FT-IR, ^{1}H NMR techniques.

1.2.1. Synthesis of DAPAPBA

DAPAPBA was synthesized according to a reported procedure[1-3]by Knoevenagel condensation reaction between 4-(dianisyl phenylamino)benzaldehyde and 2,6-dimethyl-4H-pyran-4-ylidene)pyrimidine-trione (PBA) in toluene Yield: 45%. m.p. above 300 °C,FT- IR (cm^{-1}): (KBr): 3299, 3180, 1592, 1509, 1390, 1235, 1110, 1069, 991, 700. ^{1}H NMR (DMSO d_6) δ (ppm): 10.481 (s. 1H,-PBA), 8.8723 (s, 1H, -PBA), 7.7625 (d, 1H, J = 14.76 Hz,-vinylic), 7.621 (d, 2H), 7.278 (d, 4H), 6.99 (d, 1H, J = 14.6 Hz,-vinylic),6.958 (d, 4H), 6.707 (d,2H), 3.76 (s, 6H).

1.2.2. Synthesis of TAPBA

TAPBA was synthesized according to a reported procedure[1-3]by Knoevenagel condensation reaction between 4-(diphenylamino)benzaldehyde and 2,6-dimethyl-4H-pyran-4-ylidene)pyrimidine-trione (PBA) in toluene Yield: 55%. m.p. above 300 °C,FT- IR (cm^{-1}):

(KBr): 3310, 3180, 1598, 1390, 1328, 1105, 1069, 997, 700. ^{1}H NMR (DMSO d_6) δ (ppm): 10.593 (s. 1H,-PBA), 8.830 (s, 1H, -PBA), 7.790 (d, 2H), 7.747 (d, 1H, J = 16 Hz,-vinylic), 7.425 (t, 3H), 7.406 (d, 1H), 7.199 (d, 1H, J = 15.6 Hz,-vinylic),7.178 (d, 4H), 6.979 (d,4H).

1.2.3. Synthesis of EAPBA

EAPBA was synthesized according to a reported procedure[1-3]by Knoevenagel condensation reaction between 4-(diethylamino)benzaldehyde and 2,6-dimethyl-4H-pyran-4-ylidene)pyrimidine-trione (PBA) in toluene Yield: 40%. m.p. above 300 °C,. FT- IR (cm^{-1}): (KBr): 3310, 3185, 1598, 1396, 1339, 1110, 1074, 705. ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm): 8.69(s, 1H, -PBA), 7.96(s, 1H, PBA), 7.426 (d, 1H, J = 16.4 Hz,-vinylic),7.39 (d, 2H), 6.61 (d, 2H), 6.56 (d, 1H, J = 15.6 Hz,-vinylic),3.35 (q, 4H), 1.144 (t, 6H).

1.2.4. Synthesis of CAPBA

CAPBA was synthesized according to a reported procedure[1-3]by Knoevenagel condensation reaction between 9-(2-ethylhexyl)-9H-carbazole-3-carbaldehyde and 2,6-dimethyl-4H-pyran-4-ylidene)pyrimidine-trione (PBA) in toluene Yield: 60%. m.p. above 300 °C, FT- IR (cm^{-1}) (KBr): 3299,1592, 1385, 1348, 1213, 1110, 1063, 991, 913, 851, 804, 705, 596. ^{1}H NMR (400MHz, DMSO d_6) δ (ppm):10.574 (s, 1H, -PBA), 8.931 (s, 1H, -PBA), 8.840 (s, 1H), 8.339 (d, 1H), 8.124(d, 1H), 8.110 (d, 1H, J = 15.6 Hz,-vinylic),8.119 (d, 1H), 7.67 (d, 1H), 7.58 (t, 1H), 7.42 (d, 1H, J = 16 Hz,-vinylic),7.34 (t,1H), 4.386 (d, 2H), 2.087 (t, 1H), 1.391 (m,4H), 1.244 (m,4H), 0.948(t, 3H), 0.846 (t, 3H).

1.2.5. Synthesis of DAPAPTBA

DAPAPTBA was synthesized according to a reported procedure[1-3]by Knoevenagel condensation reaction between 4-(dianisyl phenylamino)benzaldehyde and 2,6-dimethyl-4H-pyran-4-ylidene)-2-thioxodihydropyrimidine-dione (PTBA) in toluene Yield: 40%. m.p. above 300 °C,FT- IR (cm^{-1}): (KBr):3428, 3186, 3107, 2929, 1589, 1504, 1446, 1330, 1240, 1137, 1031, 823. ^{1}H NMR (DMSO d_6) δ (ppm): 11.727 (s. 1H,-PBA), 8.777 (s, 1H, -PBA), 7.73 (d, 1H, J = 16.8 Hz,-vinylic), 7.687 (d, 2H), 7.175 (d, 4H), 7.079 (d, 1H, J = 16.24 Hz,-vinylic),7.019 (d, 4H), 6.754 (d,2H), 3.182 (s, 6H).

1.2.6. Synthesis of TAPTBA

TAPTBA was synthesized according to a reported procedure[1-3]by Knoevenagel condensation reaction between 4-(diphenylamino)benzaldehyde and 2,6-dimethyl-4H-pyran-4-ylidene)-2-thioxodihydropyrimidine-dione (PTBA) in toluene Yield: 45%. m.p. above 300 °C,FT- IR (cm^{-1}): (KBr): 3437, 3177, 3095, 1585, 1483, 1446, 1326, 1278, 1137, 808. ^{1}H NMR

(400MHz, $CDCl_3$) δ (ppm): 8.792 (s. 1H,-PBA), 8.688 (s, 1H, -PBA), 7.474 (d, 1H, J = 15.6 Hz,-vinylic), 7.331 (t, 2H), 7.238 (d, 4H), 7.094 (d, 6H), 7.056(t, 2H), 6.961 (d, 1H), 6.712 (d, 1H, J = 16 Hz,-vinylic).

1.2.7. Synthesis of EAPTBA

EAPTBA was synthesized according to a reported procedure[1-3]by Knoevenagel condensation reaction between 4-(diethylamino)benzaldehyde and 2,6-dimethyl-4H-pyran-4-ylidene)-2-thioxodihydropyrimidine-dione (PTBA) in toluene Yield: 40%. m.p. above 300 °C,. FT- IR (cm^{-1}): (KBr):3423, 2968, 1590, 1520, 1441, 1348, 1143, 1073. ^{1}H NMR (400MHz, (DMSO d_6) δ (ppm):11.66 (s, 1H, -PBA), 8.738(s, 1H, PBA), 7.752 (d, 1H, J = 16 Hz,-vinylic), 6.969 (d, 1H, J = 15.6 Hz,-vinylic),6.788 (d, 2H), 6.766 (d, 2H), 1.542 (q, 4H), 1.189 (t, 6H).

1.2.8. Synthesis of CAPTBA

CAPBA was synthesized according to a reported procedure[1-3]by Knoevenagel condensation reaction between 9-(2-ethylhexyl)-9H-carbazole-3-carbaldehyde and 2,6-dimethyl-4H-pyran-4-ylidene)-2-thioxodihydropyrimidine-dione (PTBA) in toluene Yield: 60%. m.p. above 300 °C, FT- IR (cm^{-1}) (KBr):3418, 3105, 2925, 2863,1604, 1510, 1452, 1349, 1138, 791. ^{1}H NMR (400MHz, DMSO d_6) δ (ppm):11.725 (s, 1H, -PBA), 8.906 (s, 1H, -PBA), 8.856 (s, 1H), 8.811 (d, 1H), 8.641(d, 1H), 8.252 (d, 1H), 8.204 (d, 1H), 8.054(d, 1H, J = 15.6 Hz,-vinylic),7.653 (m, 1H), 7.611 (m, 1H), 7.493 (t,1H), 7.36 (d, 1H, J = 16 Hz,-vinylic),7.298 (m,1H), 4.304 (d, 2H), 1.877 (m, 1H), 1.391 (m,2H), 1.244 (m,4H),1.181 (t,2H), 0.863 (t, 3H), 0.781 (t, 3H).

1.3 Cyclic voltammogram

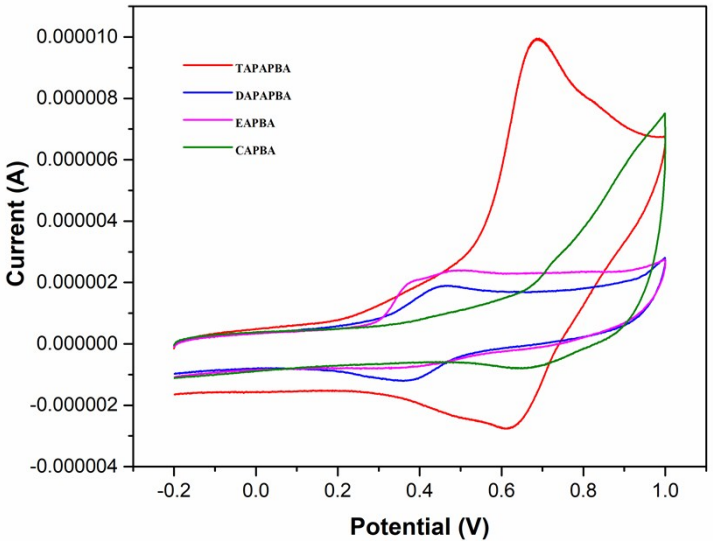

Figure S1 Cyclic voltammogram of PBA based molecules

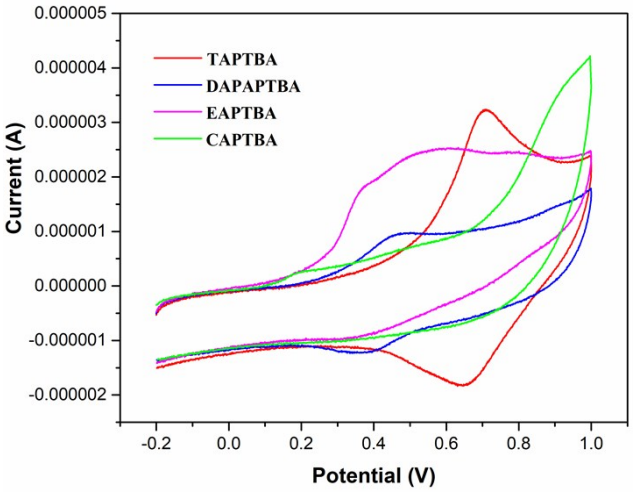

Figure S2 Cyclic voltammogram of PTBA based molecules

Reference

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