

Supporting Information

Ambipolar Organic Semiconductors with Cascades of Energy Levels for Generating Long-Lived Charge Separated States: A Donor-Acceptor₁-Acceptor₂ Architectural Triarylamine Dye

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1. General Information

Computational details. The geometry optimizations of the molecules were carried out using the three-parameter exchange functional of Becke and correlation functional of Lee, Yang and Parr (B3LYP)¹ with the 6-31+G(d,p) basis set in toluene without any symmetry constraints. The polarized continuum model (PCM) framework was used to describe the solvent interaction of the system.² The SCF convergence was 10^{-8} a.u.; the gradient and energy convergence was 10^{-4} a.u. and 10^{-5} a.u., respectively. All the calculations were performed using the Gaussian09 package.³ In order to confirm the optimized geometry is a global minimum; frequency calculations at the same level were performed.

NMR Spectrometry. ¹H NMR spectra and ¹³C NMR spectra were obtained on a VARIAN INOVA 500MHz spectrometer and the testing temperature was 25°C. The ¹H-¹H cosy spectra were obtained on a VARIAN INOVA 400MHz spectrometer and the testing temperature was 25 °C.

Mass Spectrometry. The ESI mass spectra were obtained on a Thermo Fisher LCQ Deca XP MAX mass spectrometer. MALDI-TOF mass spectra were obtained on a Bruker Autoflex tof/tofIII mass spectrometer.

UV-Vis Spectroscopy in Solution. The absorption spectra were taken on a Thermo Spectronic, Helios Gamma spectrometer. Quartz cells with a path length of 1 cm were utilized to observe absorption in the UV region.

Fluorescence Spectroscopy in Solution. The fluorescence spectra were recorded on a Varian CARY ECLIPSE fluorospectrophotometer.

Cyclic Voltammetry. The electrochemical properties were measured using a BAS 100W electrochemical analyzer utilizing the three-electrode configuration with a glassy carbon electrode as the working electrode, Ag/AgNO₃ electrode as the reference electrode and platinum as the auxiliary electrode and calibrated using a ferrocene/ferrocenium redox couple as the external standard prior to the measurements. The scan rate was 30 mV/s. The dichloromethane containing 0.1 mol/L tetra-butylammonium hexafluorophosphate (TBAPF₆) was employed as the medium for the cyclic voltammetric determination. The compound concentrations were 5×10^{-3} mol/L.

Time-Correlated Single Photon Counting (TC-SPC). Excitation of the samples was done with picosecond diode lasers (Horiba Jobin Yvon Instruments) at 366 nm (1.2 ns pulses) or 457nm (1.2 ns pulses). The laser's pulse energy was ca. 15 pJ and attenuated (often more than an order of magnitude) to the desired count rate of ca. 1% or less of the excitation frequency. A cooled (ca. -40°C) Hamamatsu MCP- photomultiplier R3809U 51 was used for detection of single photons, and the signal passed through a discriminator (Ortec 9307) and into a TAC (Ortec 566, 100 ns range used). The electrical trigger signal from the laser was also passed through a discriminator (Tennelec TC454) and on to the TAC (Ortec 566). The TAC output was read by a DAQ-1 MCA computer card using 1024 channels and collected with Horiba Jobin Yvon Data Station 2.5. Measurements were done in reverse mode at 5 MHz and under magic angle polarisation. A cut-off filter, GG400 (Excitation at 366nm) or GG515 (Excitation at 457nm), was used to block stray excitation light. A dilute solution of Ludox was used to record the instrument response function without any filter for solution measurements. No monochromator was used, i.e. all wavelengths transmitted by the cut-off filter were collected. The dye concentrations were 5×10^{-6} mol/L and the solutions were bubbled with argon for 30 min before the measurements.

Nanosecond Transient Absorption Spectroscopy. Nanosecond transient absorption measurements were performed on a LP-920 laser flash photolysis setup (Edinburgh).

Excitation at 410 nm and 500 nm with a power of 2.0 mJ per pulse from a computer-controlled Nd:YAG laser/OPO system from Oportek (Vibrant 355 II) operating at 10 Hz was directed to the sample at the excitation wavelength. The laser and analyzing light beam pass perpendicularly through a 1 cm quartz cell. The complete time-resolved spectra were obtained using a gated CCD camera (Andor iSTAR); the kinetic traces were detected by a Tektronix TDS 3012B oscilloscope and a R928P photomultiplier and analyzed by Edinburgh analytical software (LP920). All samples used in the flash photolysis experiments were bubbled with argon for 30 min before the measurements. The compound concentrations were 1×10^{-5} mol/L.

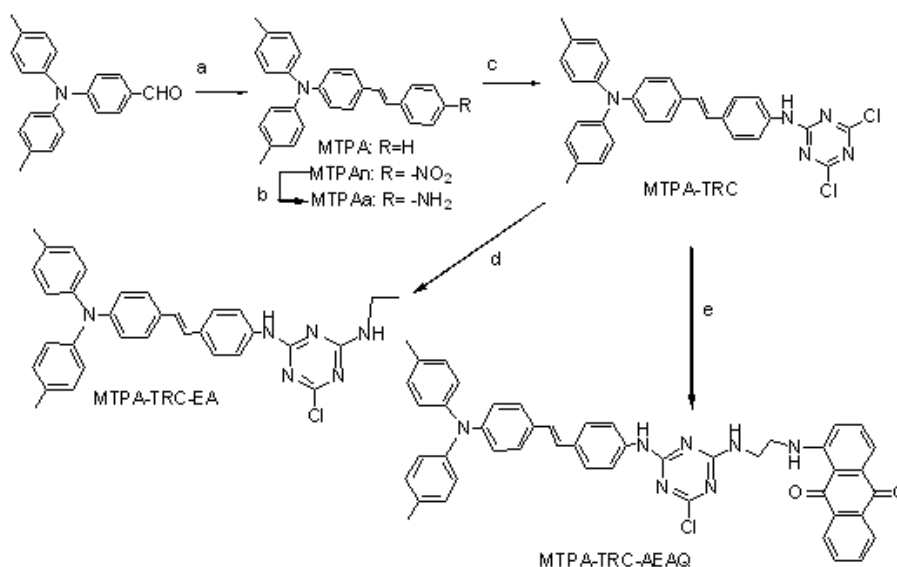
Assembly of Single-layer Organic Solar Cells. The single-layer organic solar cells were fabricated by placing MTPA-TRC-AEAQ in between ITO and Ag electrodes. The ITO-coated glass substrate was first cleaned with detergent, ultrasonicated in water, washed with acetone and isopropyl alcohol, and then dried overnight in an oven at 50°C under a vacuum of about 3×10^{-6} Torr. A film of MTPA-TRC-AEAQ was prepared on the surface of ITO layer by spin coating from its tetrahydrofuran solutions and then a cleaned Ag substrate was covered onto this film. As-fabricated solar cells were subsequently placed in a vacuum atmosphere of about 3×10^{-6} Torr for 3 h to remove the trace amounts of the solvent. All these procedures were carried out under an atmosphere of dry nitrogen. The active area of devices was 1 cm² and the thickness of the film was about 250 nm.

Photovoltaic Characteristic Determinations. The current density-Voltage (J-V) characteristic of obtained solar cells was measured using solar simulator (Zolix) under AM 1.5 G (100 mW/cm²), which was adjusted using a calibrated Si solar cell (National Institute of Metrology), and recorded with a computer-controlled digital source meter (Keithly 2400). The incident photon-to-current efficiency (IPCE) spectra were measured as a function of the wavelength from 350 to 600 nm using a specially designed IPCE system (Newports).

2. Synthetic procedures and characterization data

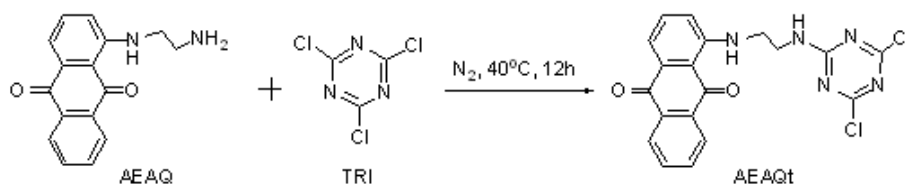
Materials. Benzyl triphenylphosphonium bromide (BTB), nitrobenzyl triphenylphosphonium bromide (NTB), 4-(N, N-bis(4-methylphenyl)amino) benzaldehyde (MAB), and 1-(2-aminoethylamino)anthraquinone (AEAQ) were prepared according to the literatures.^{4,5} The synthetic pathways of the dyes were illustrated in Scheme S1 and S2. All reagents and solvents were in reagent grade and further purified by the standard methods if necessary. All synthetic procedures were carried out under an atmosphere of dry nitrogen or dry argon unless otherwise indicated.

Scheme S1. Synthesis scheme of the dyes.



- a) N₂, BTB/NTB, NaH, 80°C, 2h; b) N₂, SnCl₂·2H₂O, 90°C, 8h; c) N₂, cyanuric chloride, 0°C, 10min; d) N₂, ethylamine, 25°C, 5min; e) N₂, AEAQ, 40°C, 12h.

Scheme S2. Synthesis reaction of AEAQt.



Synthesis of MTPA. BTB (0.38g, 0.88mmol) and NaH (0.10g, 4mmol) were dispersed in absolute THF (40mL) and the suspension was stirred at room temperature for 1h. Then 4-(N, N-bis(4-methylphenyl) amino) benzaldehyde (0.24g, 0.80mmol) dissolved in absolute THF 10mL was added into the suspension. Afterwards the suspension was refluxed at 80°C for 2h. The suspension was filtered and the solid was washed with THF (20mL). Then the combined filtrates were concentrated by rotatory evaporation. The product was further purified by column chromatography on silica gel using cyclohexane / dichloromethane (4:1 v/v) as the eluent. A yellow solid was obtained (0.27g, 90.0%); HRMS (ESI): m/z =

376.2054 [(M+H)⁺] (calcd for C₂₈H₂₆N⁺: m/z = 376.2060). ¹H NMR (CDCl₃, 500Hz): δ 7.51-7.50 (d, J = 7.5Hz, 2H), 7.38-7.34 (m, 4H), 7.26-7.23 (m, 1H), 7.10-6.97 (m, 12H), 2.34(s, 6H).

Synthesis of MTPAn. The procedures were the same as that of MTPA except that BTB was replaced by NTB (0.42g, 0.88mmol). A red solid (0.28g, yield: 83.3%) was obtained by column chromatography. mp = 156.5-157.5°C; HRMS (ESI): m/z = 421.1911[(M+H)⁺] (calcd for C₂₈H₂₅N₂O₂⁺: m/z = 421.1911). ¹H NMR (CDCl₃, 500Hz): δ 8.21-8.19 (d, J = 8.5Hz, 2H), 7.59-7.58 (d, J = 9Hz, 2H), 7.39-7.37 (d, J = 8.5Hz, 2H), 7.22-7.19 (d, J = 16Hz, 1H), 7.12-7.10 (d, J = 8Hz, 4H), 7.05-7.03 (d, J = 8Hz, 4H), 7.01-6.97 (m, 3H), 2.35(s, 6H); ¹³C NMR (CDCl₃, 100.6MHz): 149.0, 146.3, 144.7, 144.5, 133.4, 133.1, 130.0, 128.9, 127.9, 126.4, 125.2, 124.1, 123.6, 121.4, 20.8.

Synthesis of MTPAa. MTPAn (0.10g, 0.23mmol) was dissolved in absolute ethanol (40mL) and the solution was stirred at room temperature until it turned into dark red. Then SnCl₂·2H₂O (0.23g, 1mmol) was added into the solution. Afterwards the suspension was refluxed at 90°C for 8h. After filtration, the solid was washed with absolute ethanol (20mL). Then the combined filtrates were condensed by rotary evaporation. The product was further purified by column chromatography on silica gel using cyclohexane / dichloromethane (3:2 v/v) as the eluent to yield a pale yellow solid (0.085g, 91.8%). HRMS (ESI): m/z = 391.2174[(M+H)⁺] (calcd for C₂₈H₂₇N₂⁺: m/z = 391.2169). ¹H NMR (CDCl₃, 500Hz), δ: 7.33-7.32 (d, J = 8Hz, 4H), 7.08-7.07(d, J = 8Hz, 4H), 7.02-6.99 (m, 6H), 6.93-6.90 (d, J = 16.5Hz, 1H), 6.89-6.86 (d, J = 16.5Hz, 1H), 6.72-6.71 (d, J = 7.5Hz, 2H), 4.34-4.31 (m, 2H), 2.33(s, 6H).

Synthesis of MTPA-TRC. Cyanuric chloride (0.073g, 0.40mmol) was first dissolved in absolute acetone (20 mL) and then the solution was cooled down to 0°C. MTPAa (0.16g, 0.40mmol) was added into the solution, followed by a stirring at 0°C for 10 min. Then the solution was warmed to and then kept stirring at room temperature for 30 min. Afterwards the solvent was removed by rotary evaporation and the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (3:1 v/v) as the eluent to yield a yellow solid (0.21g, 97.5%). mp>300°C; HRMS (ESI): m/z = 538.1560[(M+H)⁺] (calcd for C₃₁H₂₆Cl₂N₅⁺: m/z = 538.1560). ¹H NMR (CDCl₃, 500Hz): δ 7.55-7.50 (m, 4H), 7.36-7.34 (d, J = 8.5Hz, 2H), 7.09-7.07 (d, J = 8.5Hz, 4H), 7.05-6.93 (m, 9H), 2.33 (s, 6H).

Synthesis of MTPA-TRC-EA. Ethylamine (0.0068 g, 0.15 mmol) was added to the absolute THF (20mL) solution of MTPA-TRC (0.08g, 0.15mmol). The mixture was stirred at 25°C for 5min and then the solvent was removed by rotary evaporation. The residue was purified by column chromatography on silica gel using dichloromethane/ethyl acetate (20:1 v/v) as the eluent and a red solid was yielded (0.078g, 95.2%). mp>300°C; HRMS (ESI): m/z = 547.2376[(M+H)⁺] (calcd for C₃₃H₃₂ClN₆⁺: m/z = 547.2371). ¹H NMR (CDCl₃, 500Hz): δ 7.48-7.44 (m, 2H), 7.35-7.33 (d, J = 8.5Hz, 2H), 7.08-6.92 (m, 15H), 4.33-4.30 (m, 1H), 3.53-3.50 (m, 2H), 2.33 (s, 6H), 0.96-0.93 (t, J = 7Hz, 3H).

Synthesis of MTPA-TRC-AEAQ. MTPA-TRC (0.08g, 0.15mmol) was dissolved in the absolute THF (20mL) and then AEAQ (0.04 g, 0.15 mmol) were added into the solution. The mixture was stirred at 40°C for 12h. Afterwards the solvent was removed by rotary evaporation and the residue was purified by column chromatography on silica gel using dichloromethane/ethyl acetate (20:1 v/v) as the eluent. A red solid was yielded (0.091g, 78.7%). Mp>300°C; MALDI-TOF (m/z): 767.264(M⁺). ¹H NMR (TDF, 500Hz): δ 9.97-9.94

(t, 1H), 8.27-8.16 (m, 2H), 7.80-7.42 (m, 9H), 7.37-7.35 (d, J = 8Hz, 2H), 7.25-7.24 (t, 1H), 7.07-6.93 (m, 13H), 3.76-3.63(m, 4H), 2.34(s, 6H).

Synthesis of AEAQt. The procedures were the same as that of MTPA-TRC except that MTPA was replaced by AEAQ (0.11g, 0.40mmol) and the eluent was changed to petroleum ether/ethyl acetate (2:1 v/v). A red solid was yielded (0.15g, 87.3%). Mp>300°C; HRMS (ESI): m/z = 414.0524[(M+H)⁺] (calcd for C₁₉H₁₅Cl₂N₅O₂⁺: m/z =414.0519). ¹H NMR (CDCl₃, 500Hz): δ 9.84 (s, 1H), 8.25-8.22 (t, J = 8.5Hz, 2H), 7.80-7.72 (m, 2H), 7.66-7.64 (d, J = 7.5Hz, 1H), 7.59-7.56 (m, 1H), 7.20-7.18 (d, J = 8.5Hz, 1H), 6.46 (s, 1H), 3.86-3.85 (m, 2H), 3.66-3.64 (m, 2H).

3. Supplementary figures

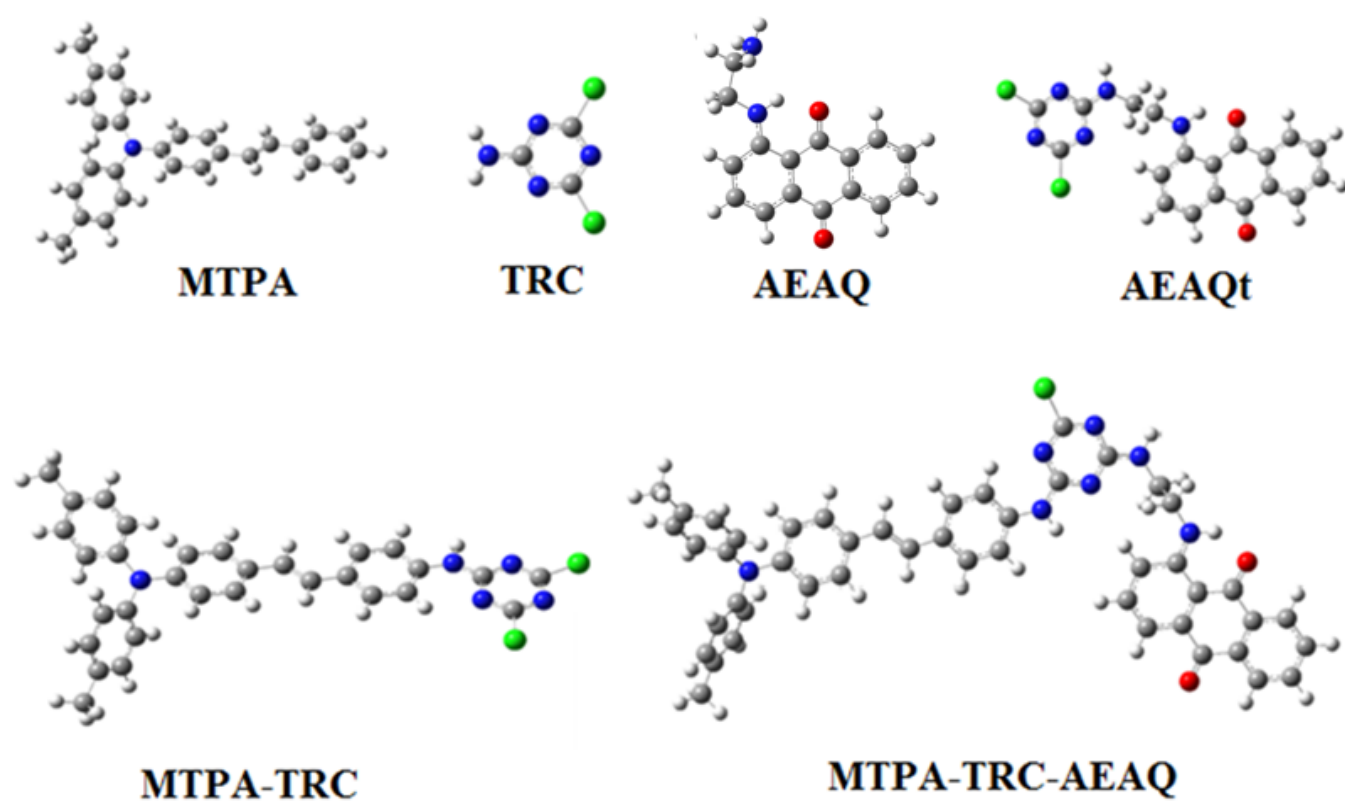


Fig. S1 Optimized structures of various compounds using B3LYP/6-31+G(d,p) in toluene. The blue, grey, red, green, and white balls represent nitrogen, carbon, oxygen, chloride, and hydrogen atoms, respectively.

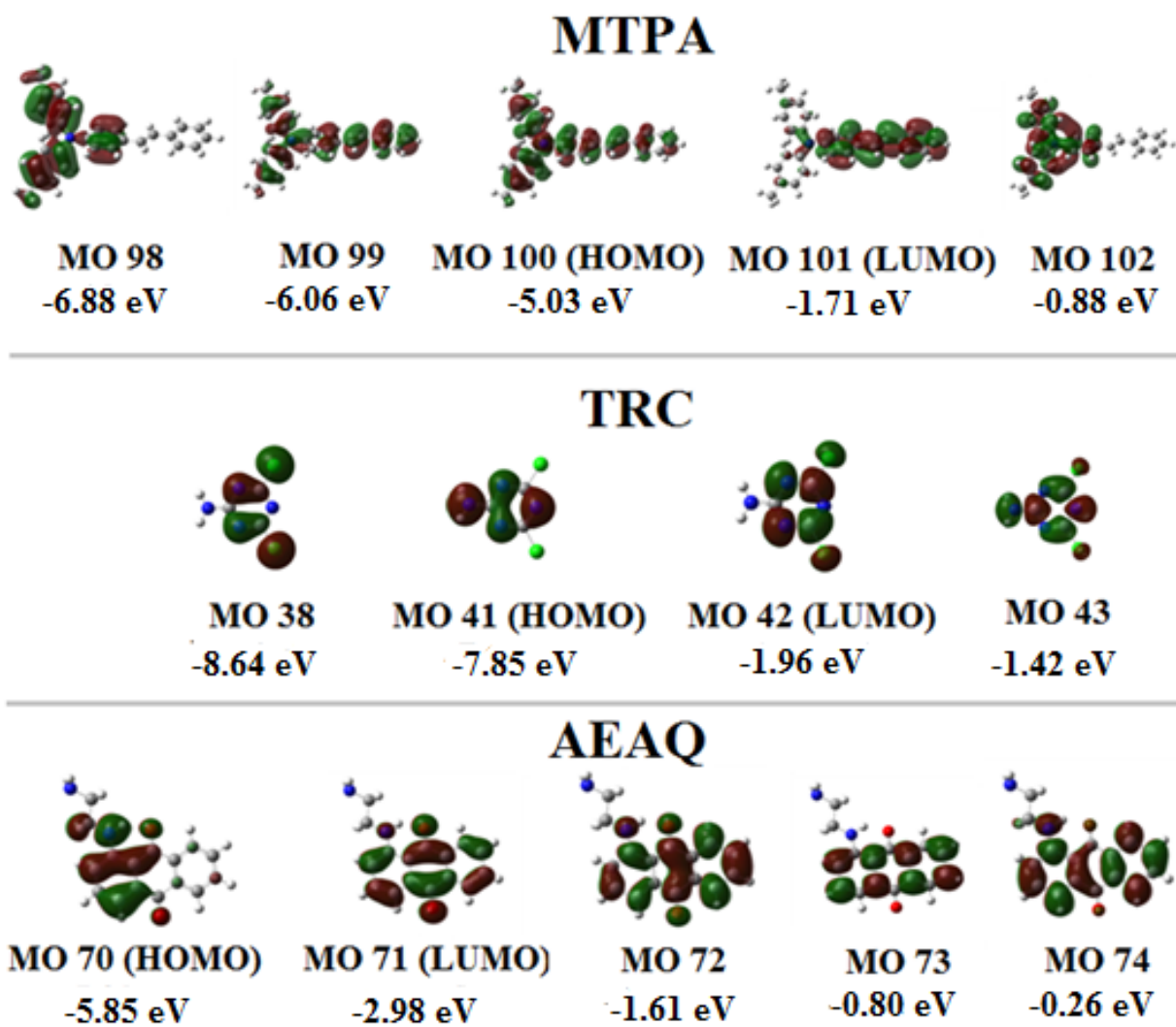


Fig. S2 Molecular orbitals and the corresponding energies of MTPA (upper), TRC (middle), and AEAQ (bottom) obtained using B3LYP/6-31+G(d,p) in toluene.

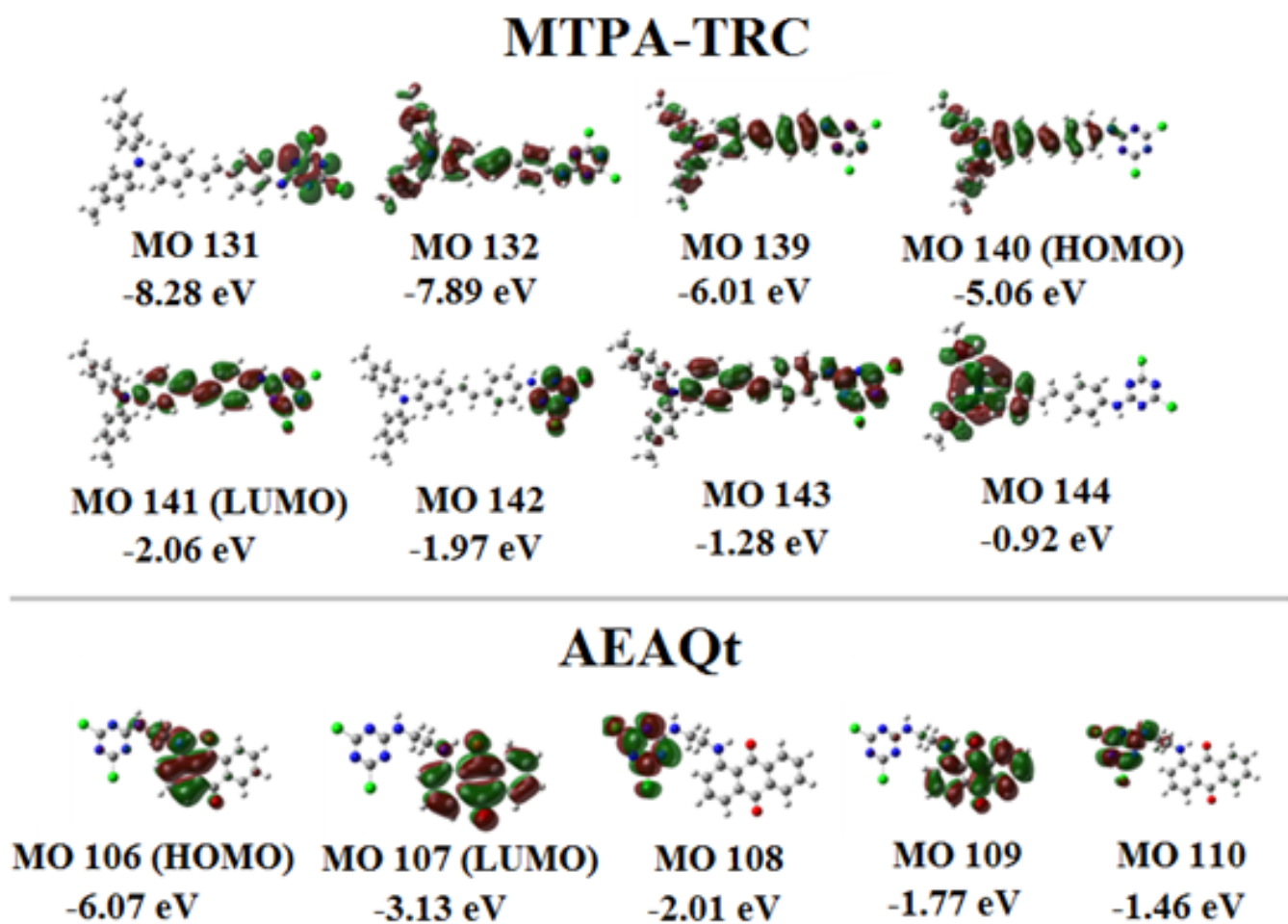


Fig. S3 Molecular orbitals and the corresponding energies of MTPA-TRC (upper) and AEAQt (below) obtained using B3LYP/6-31+G(d,p) in toluene.

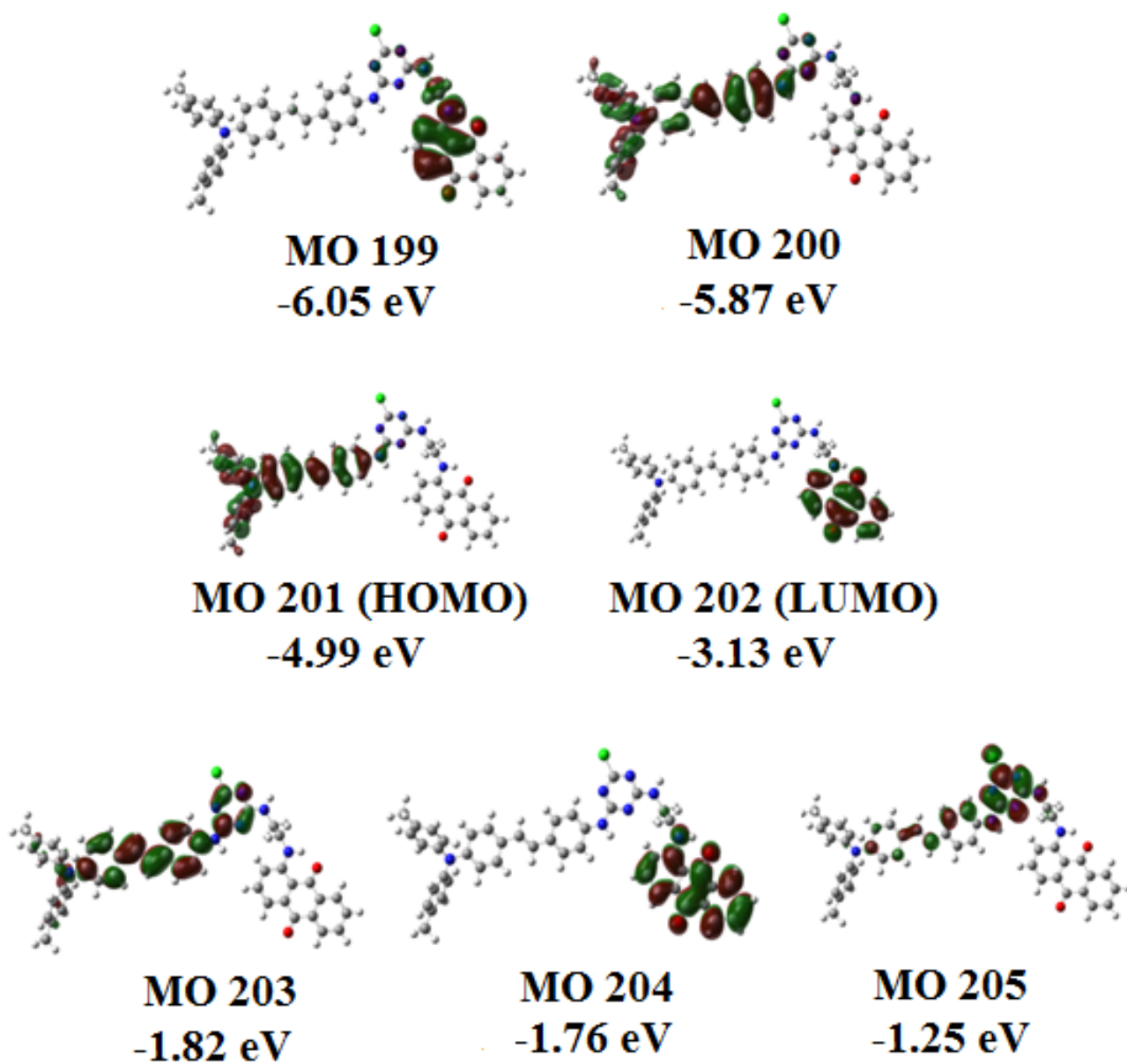


Fig. S4 Molecular orbitals and the corresponding energies of MTPA-TRC-AEAQ obtained using B3LYP/6-31+G(d,p) in toluene.

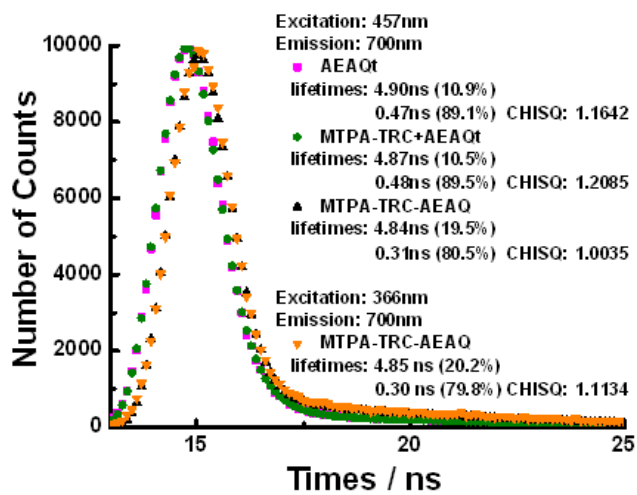
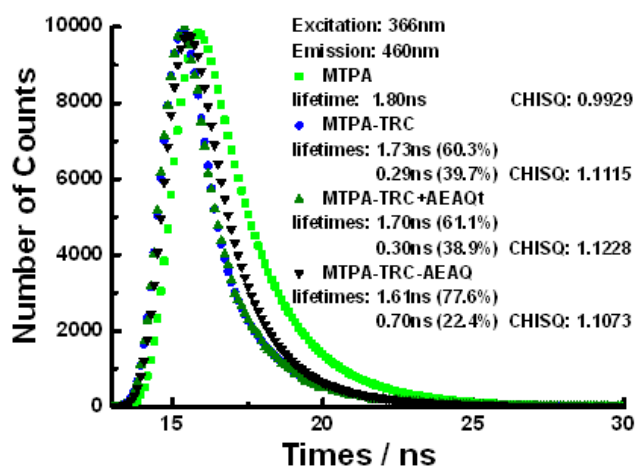


Fig. S5 Time-resolved fluorescence spectra of MTPA (green), MTPA-TRC (blue), AEAQt (magenta), MTPA-TRC-AEAQ (black/orange) and the equimolar mixture (olive) of MTPA-TRC and AEAQt in toluene. The excitation wavelength is 366 nm (upper) and 457 nm (below), respectively. The concentration is $5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$.

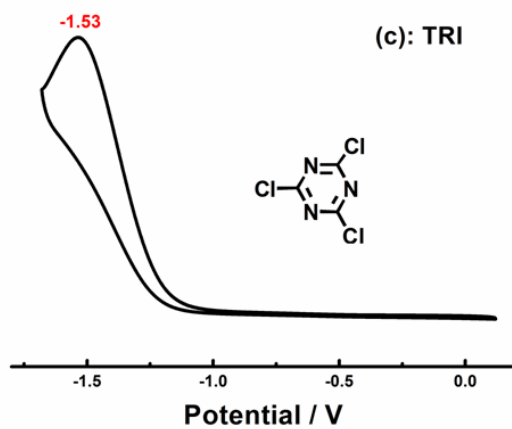
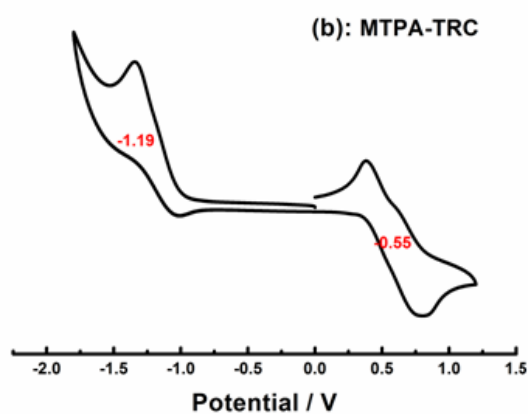
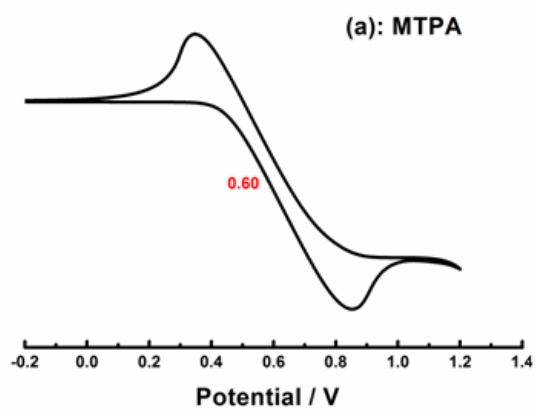


Fig. S6 Electrochemical curves of MTPA (a) and MTPA-TRC (b), and TRI (c) in dichloromethane vs Ag/Ag^+ . The concentration is $5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$.

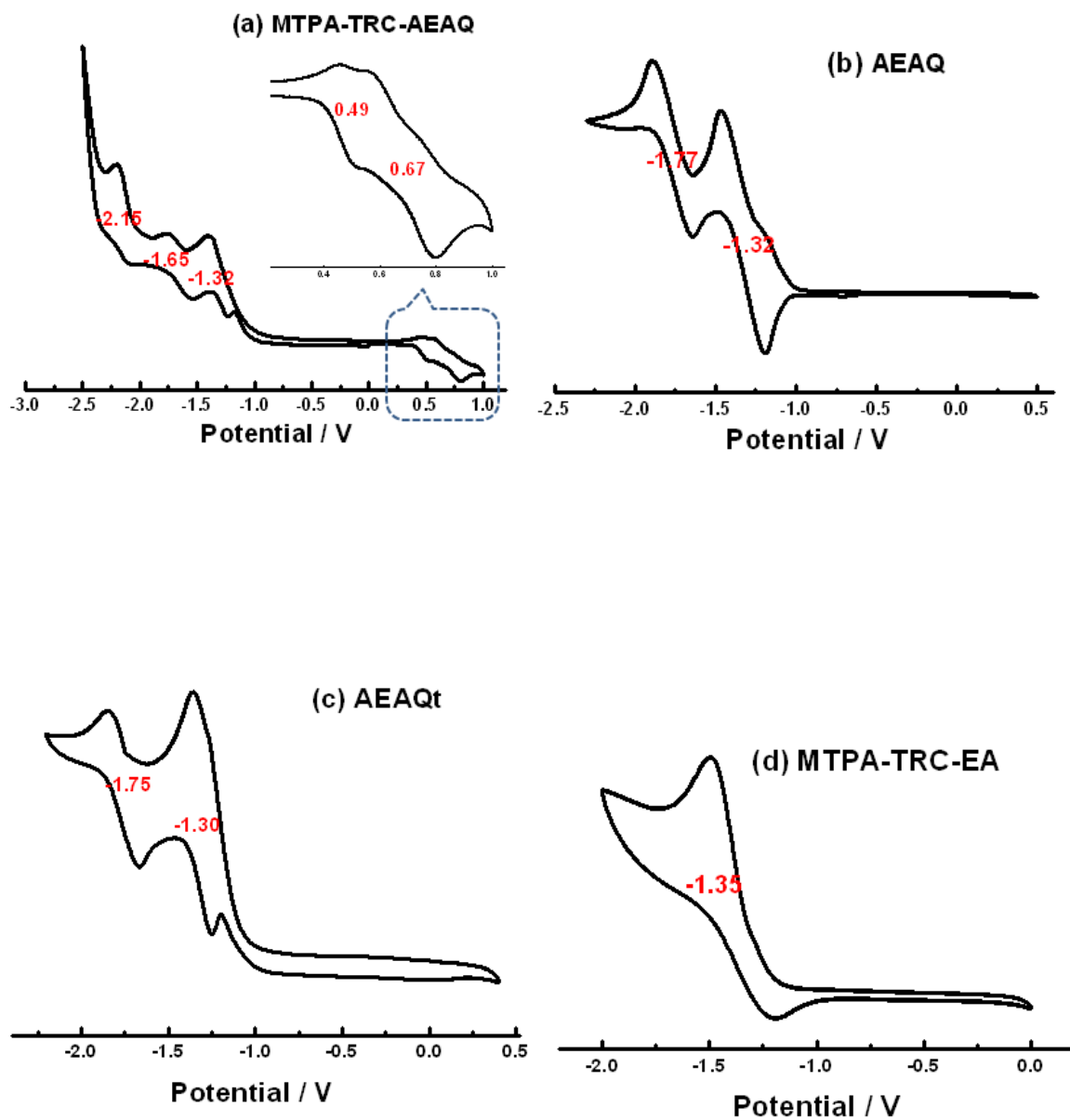


Fig. S7 Electrochemical curves of MTPA-TRC-AEAQ (a), AEAQ (b), AEAQt (c) and MTPA-TRC-EA (d) in dichloromethane vs Ag/Ag⁺. The concentration is $5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$.

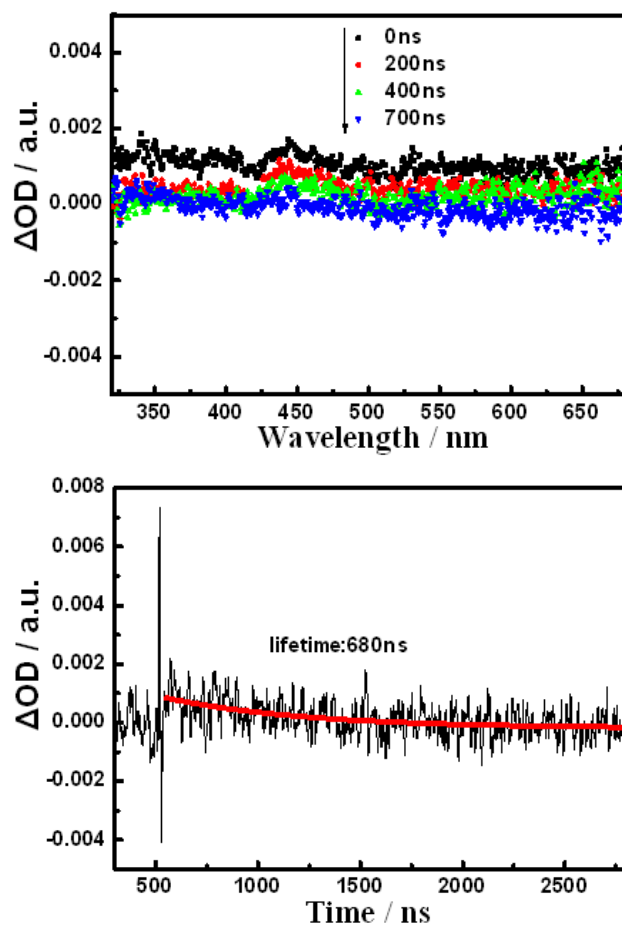


Fig. S8 Transient absorption difference spectra (a) and time-resolved absorption difference spectra at 440 nm (b) of MTPA-TRC-AEAQ ($1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) in toluene following excitation with 500 nm, 8 ns laser pulses.

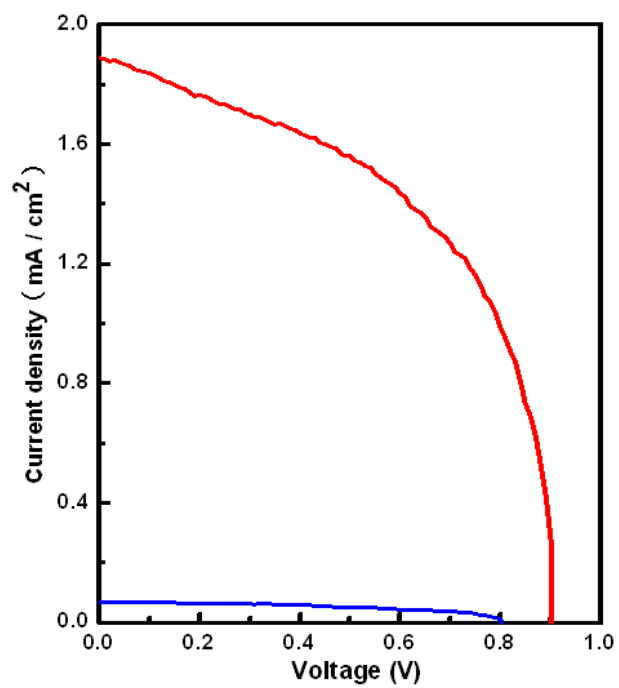


Fig. S9 J-V curves of Schottky organic solar cells ITO/MTPA-TRC-AEAQ/Ag (red) and ITO/MTPA-TRC/Ag (blue).

4. References

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