Supporting Information for

Bulk heterojunction organic solar cells based on merocyanine colorants

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Methods

Device fabrication. All devices were fabricated on commercial indium-tin oxide (ITO) coated glass. The ITO was etched with acid and subsequently cleaned using chloroform, acetone, mucasol detergent and de-ionized water in ultrasonic bath. Next, the ITO substrates were exposed to ozone for 20 minutes and immediately coated with poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Baytron P AL 4083, HC Starck; ca. 40 nm). Afterwards the samples were heat treated for 2 minutes at 110 °C to remove residual water and transferred into a N_2 glove box for the remainder of the fabrication and measurement. PCBM was obtained from Nano-C, the merocyanine dyes were synthesized according to previously reported synthetic procedures (see also Supporting Information).

The active layers were spin-coated from chlorobenzene containing the mixture of the MC and PCBM. For the MD304 solar cells, 17 vol% pyridine was added to the solution in order to improve the film quality.

The substrates were moved to a high-vacuum chamber where the top electrode was evaporated through a mask (120 nm Al), leading to seven solar cells on each substrate with an active area of 0.08 cm^2. The *JV*-characteristics of the solar cells were measured using a Keithley 2425 source measurement unit. The AM1.5 light was provided by a filtered Xe-lamp. The intensity of 100 mW cm^{-2} of the AM1.5 light was determined using a calibrated inorganic solar cell from the Fraunhofer Institute for solar research in Freiburg and a reference PCBM:P3HT cell measured by the same institution. No spectral mismatch factor was included in the calculation of the efficiency.

A Dektak surface profiler (Veeco) was used to determine the active layer thicknesses. The active layer thickness was 50 ± 5 nm. UV/vis spectra were taken with a Varian Cary 50 spectrometer.

Kelvin probe measurement. The Kelvin probe measurements were performed using a Besocke Delta phi GmbH system. The contact potential difference (*CPD*) between the investigated films, spin-coated on ITO/PEDOT:PSS substrates, and a vibrating gold grid (reference) was measured by compensating the applied voltage such that the induced oscillatory current vanished. This method does not yield absolute, but relative values and, thus, allows for quantitative comparison of the results. In earlier work we have verified that the CPD correlates with the HOMO-level of a series of triphenylamine (TPD) derivatives, which were additionally determined by *UPS*[1,2].

Cyclic voltammetry was performed on a standard commercial electrochemical analyzer (EC epsilon; BAS Instruments, UK) in a three electrode single-compartment cell under argon. Dichloromethane (HPLC grade) was obtained from J. T. Baker (Mumbai, India) and dried over calcium hydride and degassed prior to use. The supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAHFP) was recrystallized from ethanol/water and dried in high vacuum. The measurements were carried out under exclusion of air and moisture at a concentration of 10^{-4} M with ferrocene as internal standard for the calibration of the potential. Working electrode: Pt disc; reference electrode: Ag/AgCl; auxiliary electrode: Pt wire.

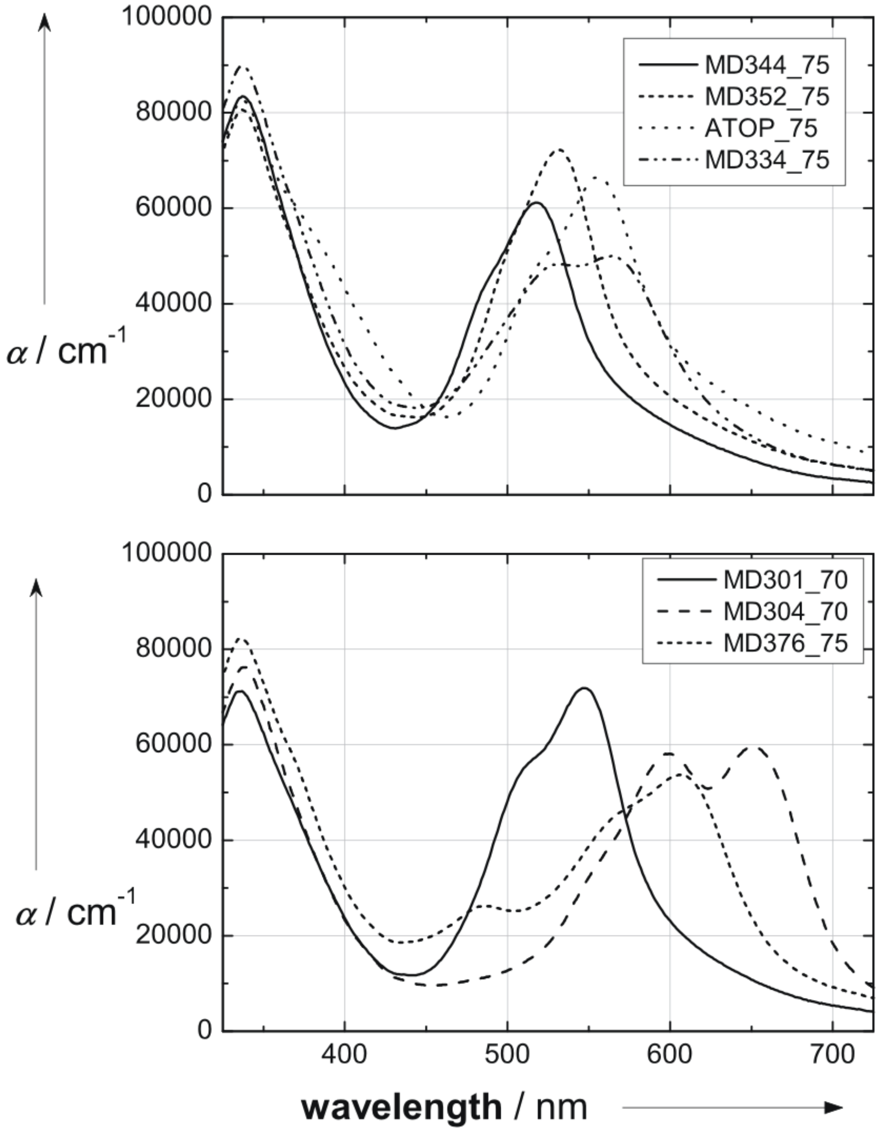


Figure S1: Absorption spectra of the investigated MC:PCBM solar cells.

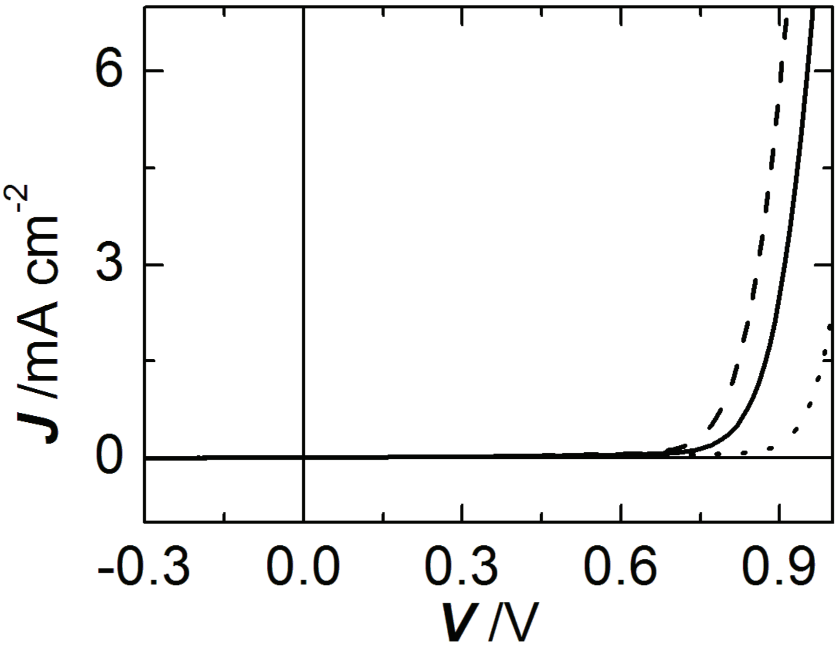


Figure S2: *JV*-characteristics of ATOP4:PCBM (solid line), MD304:PCBM (dashed line) (both 70wt% PCBM) and MD376:PCBM (dotted line) (75wt% PCBM) solar cells measured in the dark.

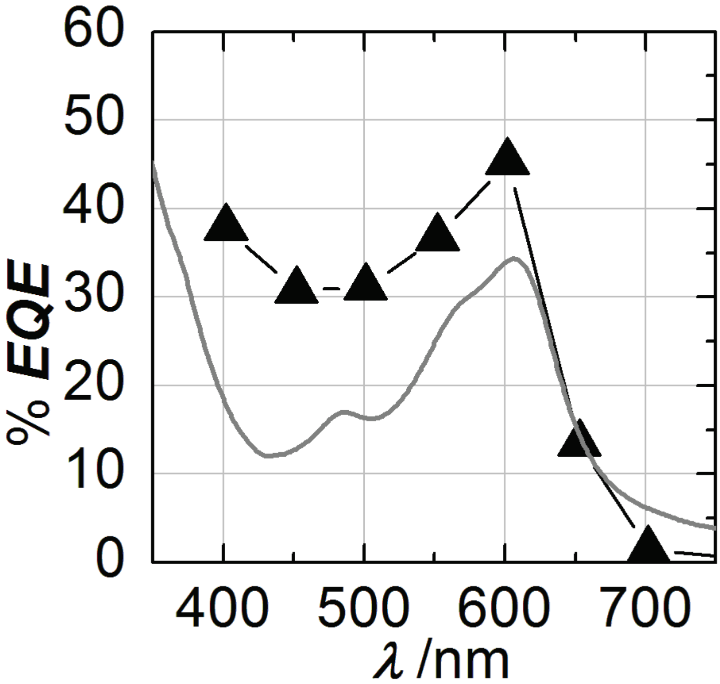
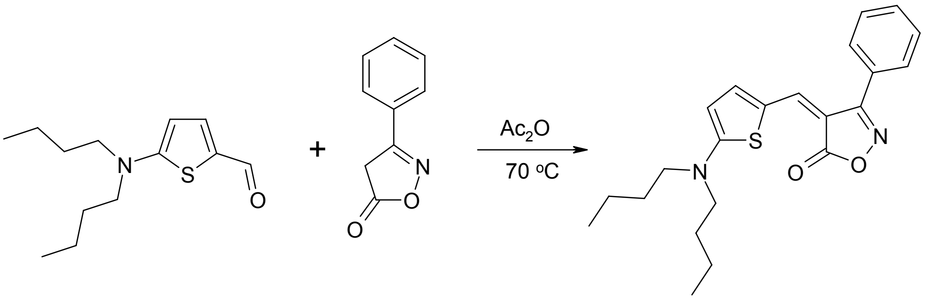


Figure S3: External quantum efficiencies of MD376-(75wt% PCBM) solar cells with Al cathode (*d* = 60 nm). The lines connecting the data points are guides to the eyes only. For comparison, the UV/Vis spectrum of the respective solar cell is shown.

Synthesis of Merocyanine Dyes:

The syntheses and characterisation data of ATOP4[3] and IDOP301[4] dyes were reported previously. The synthetic procedures and characterisation data of the remaining merocyanine dyes are given blow.

Dye MD 344:

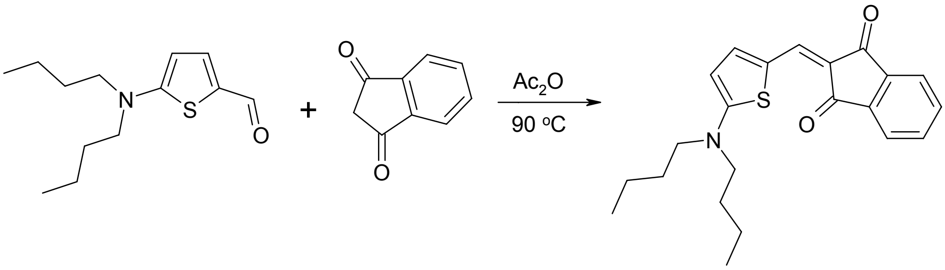


A mixture of 2-dibutylamino-5-formylthiophene (4.78 g, 20 mmol) and 3-phenyl-5-isooxazolone (3.22 g, 20 mmol) in 10 ml acetic anhydride was heated to 70 °C for 30 min under stirring. After being cooled to room temperature, the solvent was removed under vacuum and the crude product das purified by silica-gel column chromatography with toluene/ethyl acetate (9:1) as eluent. The clean fractions were combined and after removal of solvent a red oil was obtained, which became a solid in freezer after 3 days. This solid was elutriated in 100 ml of a mixture of pentane/toluene (10:1) and separated by vacuum filtration, and dried under vacuum to obtain 3.9 g (10 mmol, 50%) of merocyanine dye MD 344 as an orange powder.

M.p.: 103-104 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.58$ (m, 2H); 7.49 (m, 3H); 7.40 (s, 1H); 7.38 (d, $J = 4.9$ Hz, 1H); 6.18 (d, $J = 4.8$ Hz, 1H); 3.48 (t, $J = 7.6$ Hz, 4H); 1.70 (m, 4H); 1.39 (m, 4H); 0.98 (t, $J = 7.3$ Hz, 6H). HRMS (ESI, pos. mode, acetonitrile/chloroform 1:1): Calcd for $C_{22}H_{27}N_2O_2S$ $[M+H]^+$ (m/z) 383.17932; found 383.17878. Elemental analysis: Cacld (%) for $C_{22}H_{26}N_2O_2S$ (382.53): C, 69.08; H, 6.85; N, 7.32; S, 8.38; found: C, 68.68; H, 6.94; N, 7.44; S, 8.17.

The *Z* configuration (i.e., the thiophene ring and the carbonyl group of isooxazolone ring are on the same side of the newly created C=C double bond) of dye MD 344 is confirmed by 2D NOESY NMR spectroscopy (see Figure S1).

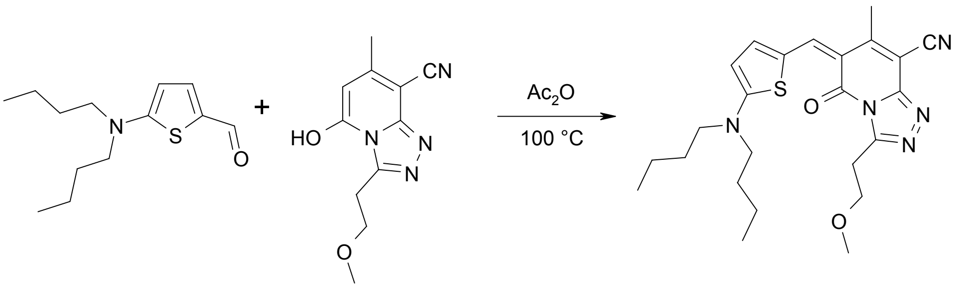
Dye MD 352:



A mixture of 2-dibutylamino-5-formylthiophene (2.39 g, 10 mmol) and 1,3-indandione (1.46 g, 10 mmol) in 5 ml acetic anhydride was heated at 90 °C for 30 min under stirring. After being cooled to room temperature, the reaction mixture was poured into 10 ml of isopropanol and the precipitate was separated by vacuum filtration and washed with isopropanol (3 x 10 ml). The obtained dark red solid was purified by silica-gel column chromatography with toluene/ethyl acetate (9:1) as eluent and dried under vacuum to obtain 1.88 g (5.1 mmol, 51%) of a red solid.

M.p.: 136-137 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.79$ (m, 2H); 7.74 (br s, 1H); 7.61 (m, 2H); 7.54 (br s, 1H); 6.17 (d, $J = 4.7$ Hz, 1H), 3.48 (t, $J = 7.7$ Hz, 4H); 1.72 (m, 4H); 1.42 (m, 4H); 0.99 (t, $J = 7.3$ Hz, 6H). HRMS (ESI, pos. mode, acetonitrile/chloroform 1:1): Calcd for $C_{22}H_{26}NO_2S$ $[M+H]^+$ (m/z) 368.16842; found 368.16788. Elemental analysis: Cacld (%) for $C_{22}H_{25}NO_2S$ (367.51): C, 71.90; H, 6.86; N, 3.81; S, 8.72; found: C, 71.38; H, 6.90; N, 3.91; S, 8.51.

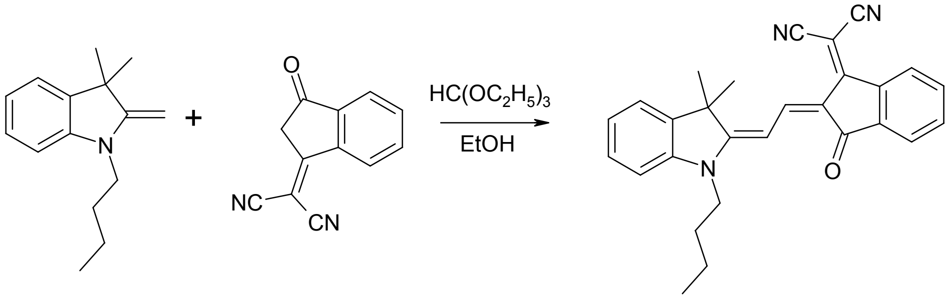
Dye MD 334:



A mixture of 2-dibutylamino-5-formylthiophene (2.39 g, 10 mmol) and the CH-acidic component (2.32 g, 10 mmol) in 10 ml of acetic anhydride was heated at 100 °C for 15 min under stirring. After being cooled to room temperature, the solvent was removed under vacuum and the crude product das purified by silica-gel column chromatography with CH_2Cl_2/MeOH (95:5) as eluent. After removal of solvent, the clean fractions were combined

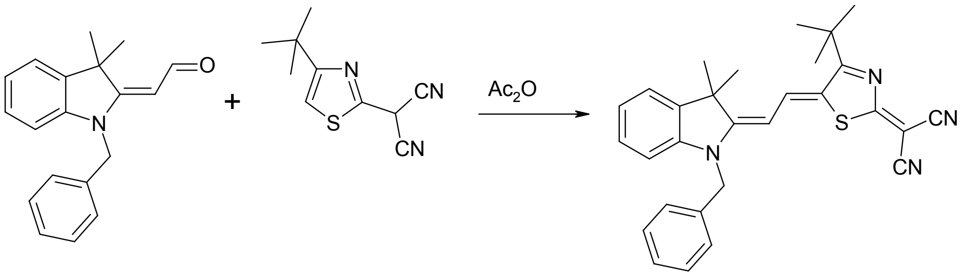
and poured into 20 ml of acetone, and subsequently precipitated by addition of *n*-hexane to obtain 4.07 g (8.97 mmol, 90%) of dye MD 334 as a violet powder.
M.p.: 179-181 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.59 (s, 1H); 7.35 (d, *J* = 5.4 Hz, 1H); 6.36 (d, *J* = 5.3 Hz, 1H); 3.93 (t, *J* = 7.2 Hz, 2H); 3.58 (m, 4H); 3.40 (s, 3H); 3.17 (t, *J* = 7.1 Hz; 2H); 2.64 (s, 3H); 1.76 (m, 4H); 1.43 (m, 4H); 1.00 (t, *J* = 7.3 Hz; 6H). HRMS (ESI, pos. mode, acetonitrile/chloroform 1:1): Calcd for $C_{24}H_{32}N_5O_2S$ $[M+H]^+$ (m/z) 454.22767; found 454.22775. Elemental analysis: Cacld (%) for $C_{24}H_{31}N_5O_2S$ (453.60): C, 63.55; H, 6.89; N, 15.44; S, 7.07; found: C, 63.50; H, 6.87; N, 15.41; S, 7.14.

Dye MD 376:



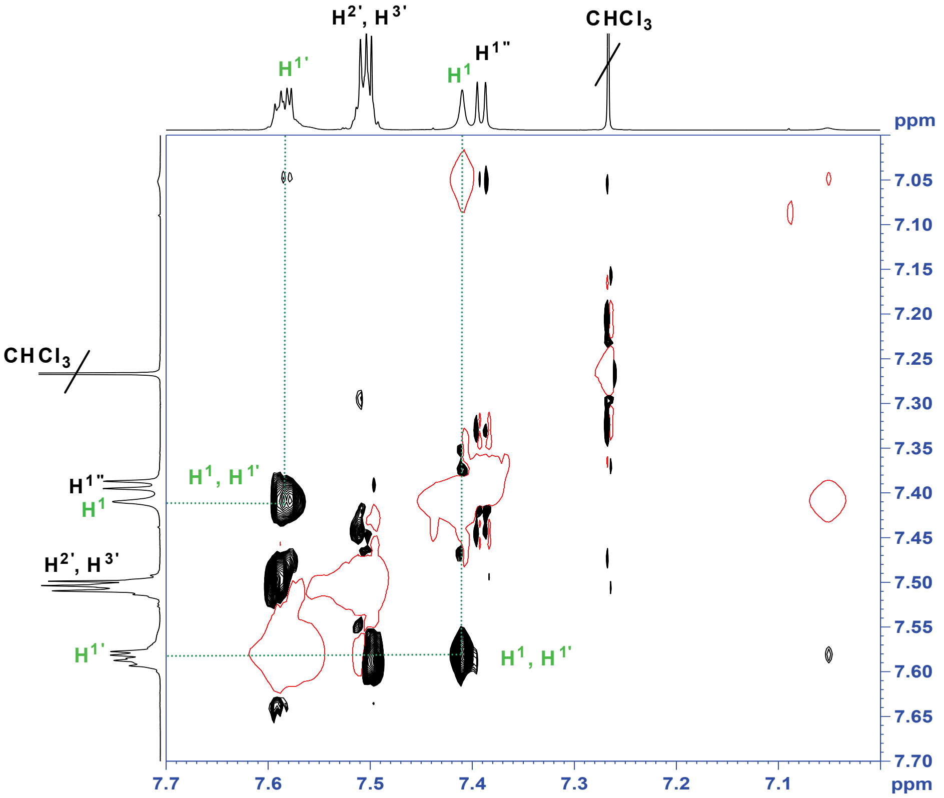
A mixture of the methylene base (2.15 g, 10 mmol), 3-dicyanovinylindan-1-one (1.94 g, 10 mmol), and orthoformic ester (2.22 g, 15 mmol) in 10 ml of ethanol was heated to reflux for 30 min. After cooling to room temperature, the solvent was removed under vacuum and crude product was purified by silica-gel column chromatography with CH_2Cl_2. After removal of solvent, the pure fractions were dissolved in 10 ml of dichloromethane and precipitated by addition of *n*-hexane to afford 2.1 g (5.0 mmol, 50%) of dye MD 376 as a green powder.
M.p.: 175-177 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.05 (d, *J* =13.9 Hz, 1H); 8.57 (m, 1H); 8.06 (d, *J* = 13.8 Hz, 1H); 7.73 (m, 1H); 7.58 (m, 2H); 7.37 (m, 2H); 7.24 (m, 1H); 7.07 (m, 1H); 4.06 (t, *J* = 7.4Hz, 2H); 1.87 (m, 2H); 1.80 (s, 6H); 1.53 (m, 2H); 1.04 (t, *J* = 7.3 Hz, 3H). HRMS (ESI, pos. mode, acetonitrile/chloroform 1:1): Calcd for $C_{28}H_{26}N_3O$ $[M+H]^+$ (m/z) 420.20759; found 420.20709. Elemental analysis: Cacld (%) for $C_{28}H_{25}N_3O$ (419.52): C, 80.16; H, 6.01; N, 10.02; found: C, 80.09; H, 6.03; N, 9.91.

Dye MD 304:



This dye was synthesised according to literature known method[5] by the condensation of 2-dicyanomethyl-3-*tert*-butylthiazole with indoline-2-ylidene aldehyde in acetic anhydride in 65% yield.

M.p.: 253-256 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.18 (d, J = 13.1 Hz, 1H); 7.36 (m, 5H); 7.20 (m, 3H); 7.01 (m, 1H); 5.53 (d, J = 13.1 Hz, 1H); 5.07 (s, 2H); 1.72 (s, 6H); 1.52 (s, 9H). HRMS (ESI, pos. mode, acetonitrile/chloroform 1:1): Calcd for $C_{29}H_{29}N_4S$ $[M+H]^+$ (m/z) 465.21129; found 465.21074.



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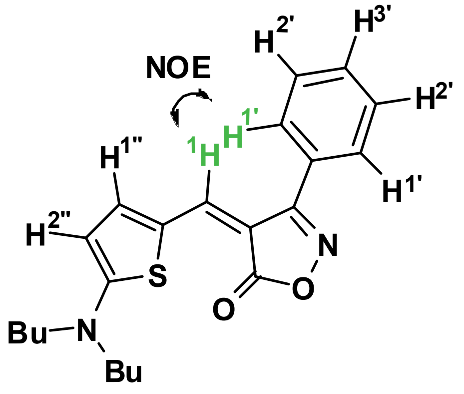

MD 344

Figure S2: NOESY spectrum (600 MHz, $CDCl_3$, room temperature) of dye **MD 344**. The significant aromatic region is shown. This spectrum reveals a strong NOE effect for the vinylic proton H^1 and ortho protons of phenyl group $H^{1'}$ (δ = 7.40 (s) and 7.58 (m) ppm, respectively), confirming the *Z* configuration since in the case of *E* configuration (i.e., the thiophene ring and the carbonyl group of isooxazolone ring are on the opposite side of the C=C double bond) there would be no NOE effect for these protons.

References

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