Influence of Merocyanine Molecular Dipole Moments on the Valence Levels in Thin Films and the Interface Energy Level Alignment with Au(111)

*S Stefan Krause 1, Matthias Stolte 2, Frank Würthner 2, and Norbert Koch 1,3

1 Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Bereich Solarenergieforschung, Albert-Einstein-Strasse 15, 12489 Berlin, Germany

2 Institut für Organische Chemie and Center for Nanosystems Chemistry, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

3 Institut für Physik, Humboldt-Universität zu Berlin, Newtonstrasse 15, 12489 Berlin, Germany

SUPPORTING INFORMATION

Synthesis of merocyanine dyes

2-[2-(1-Butyl-3,3-dimethyl-1,3-dihydro-indol-2-ylidene)-ethylidene]-indan-1,3-dione (1)

A 5 mL Ac₂O solution of (1-butyl-3,3-dimethyl-1,3-dihydro-indol-2-ylidene)-acetaldehyde (1.20 g, 4.93 mmol) and 1,3-indandione (720 mg, 4.93 mmol) was heated to 90 °C for 30 min, before the solvent was removed under vacuum. After column chromatography (first with CH₂Cl₂ 0.1% MeOH, second with CH₂Cl₂:EtOAc = 9:1), the obtained solid was dissolved in CH₂Cl₂ and precipitated with n-hexane. Yield 765 mg (2.10 mmol, 42%). Mp. 207–209 °C. ¹H NMR (CD₂Cl₂, 400 MHz): δ 8.09 (d, 3J = 14.1, 1H), 7.74 (m, 2H), 7.63 (m, 2H), 7.49 (d, 3J = 14.1,
1H), 7.34 (m, 2H), 7.16 (m, 1H), 7.02 (m, 1H), 3.97 (t, \( ^3J = 7.5 \), 2H), 1.83 (m, 2H), 1.73 (s, 6H), 1.53 (m, 2H), 1.04 (t, \( ^3J = 7.4 \), 3H). UV-vis (CH\(_2\)Cl\(_2\)): \( \lambda_{\text{max}} \) (\( \varepsilon \)) = 496 (114600 M\(^{-1}\) cm\(^{-1}\)). HRMS (ESI): Calcd for C\(_{25}\)H\(_{25}\)NO\(_2\) [M]: 371.1885, found: 371.1880. Elemental analysis: Calcd (%) for C\(_{25}\)H\(_{25}\)NO\(_2\): C, 80.83; H, 6.78; N, 3.77. Found: C, 80.66; H, 6.85; N, 3.79.

2-\{4-tert-Butyl-5-[2-(1-butyl-3,3-dimethyl-1,3-dihydro-indol-2-ylidene)-ethylidene]-5H-thiazol-2-ylidene\}-malononitrile (4)

A 4.9 mL Ac\(_2\)O solution of (1-butyl-3,3-dimethyl-1,3-dihydro-indol-2-ylidene)-acetaldehyde (1.20 g, 4.90 mmol) and 2-(4-tert-butyl-5H-thiazol-2-ylidene)-malononitrile (1.01 g, 4.90 mmol) was heated to 90 °C for 1 h. The precipitate was filtered off and washed with \( n \)-hexane and iso-propanol. Yield 965 mg (2.24 mmol, 46%). Mp. 350–352 °C. \(^1\)H NMR (CD\(_2\)Cl\(_2\), 400 MHz): \( \delta \) 8.32 (d, \( ^3J = 13.4 \), 1H), 7.38 (m, 2H), 7.23 (m, 1H), 7.07 (m, 1H), 5.64 (d, \( ^3J = 13.4 \), 1H), 3.94 (m, 2H), 1.80 (m, 2H), 1.68 (s, 6H), 1.55 (s, 9H), 1.47 (m, 2H), 1.01 (t, \( ^3J = 7.4 \), 3H). UV-vis (CH\(_2\)Cl\(_2\)): \( \lambda_{\text{max}} \) (\( \varepsilon \)) = 624 (110100 M\(^{-1}\) cm\(^{-1}\)). HRMS (ESI): Calcd for C\(_{26}\)H\(_{31}\)N\(_4\)S [M+H]: 431.2264, found: 431.2258. Elemental analysis: Calcd (%) for C\(_{26}\)H\(_{30}\)N\(_4\)S + \( \frac{1}{2} \) H\(_2\)O: C, 71.52; H, 7.08; N, 12.83; S, 7.34. Found: C, 71.61; H, 6.88; N, 12.77; S, 7.49.

This material is available free of charge via the Internet at http://pubs.acs.org.