Intramolecular Energy Transfer in a tetra-Coumarin Perylene system: influence of solvent and bridging unit on electronic properties

Johannes H. Hurenkamp,^{*a*} Wesley R. Browne,^{*a*} Ramūnas Augulis,^{*b*} Audrius Pugžlys,^{*b,c*} Paul H. M. van Loosdrecht,^{*b*} Jan H. van Esch,^{*a,d*,*} Ben L. Feringa,^{*a,**}

^aStratingh Institute for Organic Chemistry, Faculty of Mathematics and Natural Sciences, University of Groningen, Nijenborgh 4, 9747AG Groningen, The Netherlands. Fax: 0031-50-3634296; Tel: 0031-50-3634235; E-mail: j.h.vanesch@tudelft.nl, b.l.feringa@rug.nl

^bZernike Institute for Advanced Materials, Faculty of Mathematics and Natural Sciences, University of Groningen, Nijenborgh 4, 9747AG Groningen, The Netherlands.

^d present address: Photonics Institute, Vienna University of Technology, Gusshausstrasse 27/387, 1040, Vienna, Austria. ^d present address: Delft ChemTech, Technical University Delft, Julianalaan 136, 2628 BL, Delft, The Netherlands

Molecular orbital diagrams of 9, 12a and 12b, obtained using Gaussian 03 B.04 using the hybrid Hartree–Fock/density functional method (B3LYP/6-31G(d))¹





Experimental details for NMR and other measurements.

¹H NMR spectra were recorded at 400 MHz; ¹³C NMR spectra at 50.3 or 100.6 MHz. All spectra were recorded at ambient temperature, with the residual proton signals of the solvent as an internal reference. Chemical shifts are reported relative to TMS.

CI and EI mass spectra were recorded on a Jeol JMS-600 mass spectrometer in the scan range of m/z 50–1000 with an acquisition time between 300 and 900 ms and a potential between 30 and 70 V. MALDI-TOF spectra were recorded on an Applied Biosystems Voyager-DE Pro.

UV/Vis absorption spectra (accuracy ± 2 nm) were recorded on a Hewlett-Packard UV/Vis 8453 spectrometer. The fluorescence measurements were performed on a SPF-500C spectrofluorometer (SLM Aminco), and a Jobin-Yvon Fluorolog 3-22, the sharp features between $\lambda = 450$ and 500 nm in the excitation spectra are instrumental artifacts, the excitation and emission spectra are uncorrected for variations in lamp output intensity.

Quantum yields where determined using 9,10-diphenylanthracene ($\Phi_f = 0.88$, EtOH)² for **1a**, **4** and for the residual coumarin emission of **12c** (CH₂Cl₂, $\lambda_{ex} = 322$ nm). Rhodamine 101 ($\Phi_f = 1.00$, EtOH)³ was used for compounds **9** and **12a-c** (CH₂Cl₂, $\lambda_{ex} = 539$ nm). The absorbance of all measured solutions was kept < 0.1.

Electrochemical measurements were carried out on a Model 630B Electrochemical Workstation (CHInstruments). Analyte concentrations were typically 0.5-1 mM in anhydrous dichloromethane containing 0.1 M TBAPF₆ (except where stated otherwise in the text). Unless otherwise stated, a Teflon-shrouded glassy carbon working electrode (CHInstruments), a Pt wire auxiliary electrode and SCE or non-aqueous Ag/Ag+ ion reference electrode were employed. Reference electrodes were calibrated with 0.1 mM solutions of ferrocene (0.38 V versus SCE in 0.1M TBAPF₆/ CH₃CN). Solutions for reduction measurements were deoxygenated by purging with dry N₂ gas (presaturated with solvent) prior to the measurement. Cyclic voltammograms were obtained at sweep rates of between 10 mVs⁻¹±1 and 50 Vs⁻¹±1; differential pulse voltammetry (DPV) experiments were performed with a scan rate of 20 mVs⁻¹±1, a pulse height of 75 mV and a duration of 40 ms. For reversible processes the half-wave potential values are reported; identical values were obtained from DPV and CV measurements. Redox potentials are ±10 mV.

Luminescence lifetime measurements were obtained using an Edinburgh Analytical Instruments (EAI) timecorrelated single-photon counting apparatus (TCSPC) comprised of two model J-yA monochromators (emission and excitation), a single photon photomultiplier detection system model 5300, and a F900 nanosecond flashlamp (N₂ filled at 1.1 atm pressure, 40 kHz) interfaced with a personal computer via a Norland MCA card. A 400 nm cut off filter was used in emission to attenuate scatter of the excitation light (337 nm). Excitation at $\lambda = 322$ and 420 nm corresponding to emission lines of the nitrogen flash lamp. The instrument response has a FWHM of 0.89 ns, 4096 channels were used for acquisition with a peak count of 1800 in the maximum channel. Data correlation and manipulation was carried out using EAI F900 software version 5.1.3. Emission lifetimes were calculated using a single-exponential fitting function, Levenberg-Marquardt algorithm with iterative deconvolution (Edinburgh instruments F900 software). The reduced χ^2 (less then 1.1) and residual plots were used to judge the quality of the fits. Lifetimes are $\pm 5\%$. Picosecond time resolved spectra were recorded as described elsewhere.⁴

Experimental procedures for 10, 12a and 12b

(10) 1,6,7,12-tetrakis-[4'-tert-butylphenoxy]-3,4:9,10-perylenetetracarboxylic dianhydride

9 (3.77 g, 3.4 mmol) was suspended in *tert*-butyl alcohol (270 ml) in a 500 ml roundbottom flask fitted with a reflux condenser, followed by addition of water (13 ml) and KOH (26.8 g, 478 mmol). Under a dinitrogen atmosphere the mixture was stirred and heated at reflux for 24 h. Subsequently the mixture was cooled down to RT and poured into 10% HCl (aq) (800 ml) and left overnight. The precipitate was filtered off, washed with water and dried in a vacuum oven (40°C, 200 mbar). The dark red compound was used without further purification (3.03 g, 3.1 mmol, 91.2 %). ¹H NMR (400 MHz, CDCl₃) δ = 8.2 (s, 4H), 7.2 (d, J = 8.8 Hz, 8H), 6.8 (d, J = 8.7 Hz, 8H), 1.3 (s, 36H). ¹³C NMR (100.6 MHz, CDCl₃) δ = 159.73 (s), 156.35 (s), 152.27 (s), 147.97 (s), 133.38 (s), 126.86 (d), 121.39 (s), 121.32 (d), 121.30 (s), 119.30 (d), 118.57 (s), 34.39 (s), 31.38 (q). MALDI-TOF MS (MW = 638.03) m/z = 639.19 [M+].

(12a) N,N'-Bisphenyl-1,6,7,12-tetrakis-[4'-tert-butylphenoxy]-3,4:9,10-perylenetetracarboxylic diimide.

In a 100 ml roundbottom flask fitted with a reflux condenser **10** (100 mg, 0.10 mmol), aniline (1.0 g, 11 mmol) and toluene (10 ml) were heated at 120°C under a dinitrogen atmosphere for 5 d, after which the solvent was evaporated. The crude compound was dissolved in CH₂Cl₂ and extracted twice with 1M HCl (aq) and once with brine. The organic layer was dried and evaporated in vacuo. The crude product was purified using column chromatography (CH₂Cl₂/cyclohexane 3:1, SiO₂) giving the pure compound **12a** (67 mg, 0.059 mmol, 59 %). ¹H NMR (400 MHz, CDCl₃) δ = 8.19 (s, 4H), 7.48-7.36 (m, 10H), 7.18 (d, J = 8.8 Hz, 8H), 6.80 (d, J = 8.8 Hz, 8H), 1.22 (s, 36H). ¹³C NMR (100.6 MHz, CDCl₃) δ = 163.5 (s), 156.0 (s), 152.7 (s), 147.3 (s), 135.1 (s), 133.1 (s), 129.2 (d), 128.6 (d), 128.5 (d), 126.6 (d), 122.5 (s), 120.7 (s), 120.1 (d), 119.7 (s), 119.3 (d), 34.3 (s), 31.4 (t). MALDI-TOF MS (MW = 1134.48) m/z = 1134.52 [M+].

(12b) N,N'-(3,5-(piperidine-1-carbonyl)-phenyl)-1,6,7,12-tetrakis-[4'-tert-butylphenoxy]-3,4:9,10-perylenetetracarboxylic diimide.

In a 100 ml roundbottom flask fitted with a reflux condenser **10** (100 mg, 0.10 mmol), **11** (after deprotection of **14** *via* the general method described above) (126.2 mg, 0.4 mmol) and dimethylacetamide (20 ml) were heated at 130°C under a dinitrogen atmosphere. After 5 d. the reaction mixture was poured into 1M HCl (aq) and left overnight. The precipitate was filtered off and the residue washed with 1M HCl (aq) and water. The residue was taken up into MeOH/CH₂Cl₂ 1:1, dried over Na₂SO₄ and the solvent evaporated. The crude compound was purified by column chromatography (3% MeOH in CH₂Cl₂, SiO₂) giving the solid purple product (60 mg, 0.038 mmol, 38 %) ¹H NMR (400 MHz, CDCl₃) δ = 8.25 (s, 4H), 7.51 (s, 2H), 7.35 (s, 4H), 7.22 (d, J = 8.8 Hz, 8H), 6.82 (d, J = 8.7 Hz, 8H), 3.66 (s, 10H), 3.38 (s, 10H), 1.80-1.42 (m, 20H), 1.27 (s, 36H). ¹³C NMR (50 MHz, CDCl₃) δ = 168.3 (s), 163.1 (s), 156.1 (s), 152.8 (s), 147.4 (s), 137.4 (s), 134.9 (s), 133.1 (s), 128.7 (d), 126.7 (d), 125.8 (d), 122.4 (s), 120.9 (s), 120.3 (d), 119.7 (s), 119.2 (d), 48.9 (t), 43.4 (t), 31.4 (q), 26.4 (t), 25.6 (t), 24.5 (t). MALDI-TOF MS (MW = 1578.76) m/z = 1578.73 [M+].



¹H NMR spectral data of 9 and 12a-12c (400 MHz)







12c

¹ Gaussian 03, Revision B.04, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

² M. Mardelli and J. Olmsted III, *J. Photochem*. 1977, **7**, 277

³ T. Kartstens and K. Kobs, J. Phys. Chem. 1980, 84, 1871.

⁴ R. Augulis, A. Pugžlys, J. H. Hurenkamp, B. L. Feringa, J. H. van Esch and P. H. M. van Loosdrecht, manuscript submitted, 2007.