A Perylene Diimide Rotaxane: Synthesis, Structure and Electrochemically Driven De-Threading

Benjamin J. Slater,^[a] E. Stephen Davies,^[a] Stephen P. Argent,^[a] Harriott Nowell,^[b] William Lewis,^[a] Alexander J. Blake,^[a] and Neil R. Champness^{*[a]}



14746 -

FULL PAPER

Abstract: The first example of a [2]-rotaxane in which a perylene diimide acts as a recognition site has been synthesised and characterised. The interlocked nature of the compound has been verified by both NMR studies and an Xray structure determination. Electrochemical investigations confirm that the nature of the redox processes associated with the perylene diimide are modified by the complexation process and that it is possible to mono-reduce the [2]-rotaxane to give a radical anion

Keywords: electrochemistry \cdot perylene diimide \cdot redox chemistry \cdot rotaxanes \cdot X-ray structures

based rotaxane. Further reduction of the compound leads to de-threading of the macrocycle from the reduced PTCDI recognition site. Our synthetic strategies confirm the potential of PTCDI-based rotaxanes as viable targets for the preparation of complex interlocked species.

Introduction

The synthesis of interlocked species has long fascinated the chemist and many elegant studies have been reported since the original concepts of supramolecular chemistry were proposed.^[1] The field has developed significantly allowing the assembly of remarkable species with highly tuned components leading to the construction of molecular machines.^[2] In such studies components have been developed as recognition sites including a variety with redox-^[3] or photo-active^[4] properties; these include the elegant work of Sanders and co-workers who have developed the synthesis of naphthalenediimide (NDI) species in both catenanes and rotaxanes.^[5]

It is surprising therefore that the larger analogue of NDIs, N,N'-bis(alkyl)-3,4,9,10-perylene tetracarboxylic acid diimides (PTCDIs), have not be widely exploited for the formation of interlocked species. PTCDIs display useful redox properties, typically exhibiting two reversible reduction processes, are highly coloured, a property that can be tuned by chemical substituents and redox state, and are commonly fluorescent in solution, with significant quantum yields.^[6] Indeed, the only reported examples of rotaxanes including PTCDI units either use the PTCDI moiety as a stopper unit^[7] or exploit a sterically encumbered PTCDI group as part of the axle such that only the imide moieties act as recognition sites.^[8]

We have therefore developed a method for preparing a PTCDI-based rotaxane using a 'slipping' approach (Scheme 1).^[9] We targeted PTCDI derivatives without substitution around the periphery, or 'bay' region, of the perylene moiety to avoid complications with additional steric bulk and/or isomerism around the PTCDI recognition site.

- [a] Dr. B. J. Slater, Dr. E. S. Davies, Dr. S. P. Argent, Dr. W. Lewis, Prof. Dr. A. J. Blake, Prof. Dr. N. R. Champness School of Chemistry, University of Nottingham University Park, Nottingham, NG7 2RD (UK) E-mail: Neil.Champness@nottingham.ac.uk
- [b] Dr. H. Nowell Diamond Light Source, Diamond House Harwell Science and Innovation Campus Didcot, Oxfordshire OX11 0DE (UK)
- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201103090.



Scheme 1. 1) imidazole, $ZnBr_2$, 170 °C, 4 h; 2) CHCl₃/MeOH (95:5), 65 °C, 14 days.

Such unfunctionalised PTCDI derivatives are known to have low solubility in many solvents and therefore synthetic routes usually employ derivatisation to improve solubility.^[6] Imidisation of PTCDA, the corresponding dianhydride to PTCDI, proceeds only at relatively high temperatures^[10] and is therefore an unattractive step when trying to prepare sensitive species such as rotaxanes. Thus it was decided to prepare the axle, introducing groups that aid solubility and act

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

www.chemeurj.org

- 14747

as stoppers and to pursue a 'slipping' approach to rotaxane formation.

Results and Discussion

The target rotaxane was prepared by sequential synthesis of the axle molecule **1** and subsequent complexation of the macrocycle 2. Axle 1 was constructed from a PTCDI unit and two bis(4-tert-butylphenyl)(4-ethylphenyl)(4-phenoxy) methane stopper groups; the latter have proved to be effective in allowing slipping reactions in rotaxane formation.^[11] Axle 1 and an excess of macrocycle 2^[12] were dissolved in a small volume of CHCl₃/MeOH (95:5) and heated to 65°C under N_2 in a sealed pressure tube for 2 weeks (Scheme 1). The desired product 3 was isolated by column chromatography in a relatively low yield (8%). Attempts were made to improve the yield and reaction time using alternative reaction conditions involving a melt phase. The melting point of the macrocycle 2, 138°C, was exploited and it was found that heating a mixture of 1 in an excess of 2 at 160°C for 6 hours produced the desired product in yields that were still low (8%), but more acceptable given the much reduced overall reaction times.

Formation of [2]-rotaxane **3** was confirmed by NMR spectroscopy through key changes observed in the ¹H NMR spectrum (Figure 1). The typical PTCDI double doublet of $H_{a/b}$ is replaced by a broad singlet at 8.5 ppm due to the



Figure 1. The aromatic region of the ¹H NMR spectra of i) axle 1; ii) [2]-rotaxane 3 and ii) macrocycle 2 at $25 \,^{\circ}$ C.

PTCDI interacting with the macrocyclic component 2; it is likely that the macrocycle is shuttling over the PTCDI at room temperature. Macrocycle protons H₁, H₂ and H₃ all show a direct upfield shift of approximately 1 ppm and more complex profiles. Resonances associated with glycol chains of 2 are also shifted compared to the values in the free macrocycle, with the two triplets shifting upfield to 3.85 and 3.74 ppm, while the complex multiplet shifts downfield to 4.03 ppm. NOE and ROE experiments on 3 at room temperature failed to detect coupling between the axle and macrocycle, possibly owing to the fluxional nature of the molecule at this temperature, therefore low temperature VT NMR spectroscopy was carried out on 3 in a CD₂Cl₂ solution. The temperature was first lowered to 273 K and then decreased in 10 K steps to 193 K (see the Supporting Information). H_{a/b} splits at low temperature into a complex signal that is unsymmetrical, thus indicating desymmetrisation of 3 upon cooling. A series of one-dimensional ROE experiments was carried out at 193 K and through-space interactions were noted. ROESY NMR studies were therefore carried out at low temperature (see the Supporting Information). Through-space interactions were detected between a number of the resonances, notably H_1 on the macrocycle being associated with $H_{\mbox{\tiny a/b}}$ on the axle, thus indicating that 2resides on the PTCDI. Thus, we conclude from the NMR experiments that 3 exists as a [2]-rotaxane in solution with the PTCDI operating as a recognition site.

A purple single crystal of **3** was successfully grown by layering MeOH onto a solution of the compound in toluene. A single crystal X-ray diffraction study established that the structure of **3** was a [2]-rotaxane in the solid state, showing the axle 1 threaded through the macrocycle 2 and adopting a Z conformation with one stopper above the pervlene plane and one below (Figure 2a). As expected, the macrocycle naphthalene units are both involved in π - π stacking interactions with opposite sides of the PTCDI core, with centroid-to-plane separations of 3.43 and 3.49 Å. The values are similar to previously reported rotaxanes involving the macrocycle 2,^[13] although slightly longer than that reported for a related pyromellitic diimide recognition site.[5a] The closest points between the axle and macrocycle are via two pairs of C-H···O contacts (H···O=2.67, 2.79 Å; Figure 2b) between perylene hydrogen atoms and a glycol oxygen atom.

The redox behaviour of **1** and **3** was analysed by cyclic voltammetry (CV), bulk electrolysis and UV/Vis spectroelectrochemistry and that of **2** by CV only. As anticipated,^[6] **1** undergoes two chemically reversible one-electron reduction processes, at $E_{1/2} = -0.95$ and -1.10 V, versus Fc⁺/Fc, based on the PTCDI moiety (see Figure 3 a and the Supporting Information for further discussion). In contrast, the [2]-rotaxane **3** displays a single asymmetric couple ($E_{1/2} \approx -1.19$ V vs. Fc⁺/Fc) the shape of which is essentially independent of scan rate (Figure S10 in the Supporting Information) and occurs at a potential more negative than the first reduction of the parent PTCDI. The shift in potential may be rationalised by an increase in electron density on the perylene core due to proximity of electron-rich naphthyl groups of the



Figure 2. Views of a) the X-ray structure of **3** confirming the [2]-rotaxane structure; b) C–H···O interactions between the perylene core and macrocycle glycol chain. Primed atoms are related to their unprimed equivalents by the inversion symmetry operator (-x, -y, -z) and the stopper groups are omitted for clarity.

macrocycle, but the presence of a single-reduction process was unexpected and demonstrates a clear change in electrochemical properties of the PTCDI moiety as a result of complexation. Typically for PTCDI molecules, two one-electron reductions are present^[14] and the difference in potentials between the first and second reductions results from Coulombic repulsion between the added electrons acting through the π framework of the aromatic core. Therefore, the observation of a single process for 3 may result from either two one-electron reductions with no significant interactions or the presence of only a single-electron reduction process. For 1 the presence of two one-electron processes, that rapidly developed equilibrium, was confirmed by a bulk electrolysis experiment. However, the analogous experiment for 3 gave rapid electrolysis, initially to an approximately 1 electron reduced form, followed by a slow reduction characterised by an almost linear current profile (Figure S11 in the Supporting Information). Cyclic voltammograms recorded for 3 prior to electrolysis and then after a reduction-oxidation cycle indicated the presence of an additional couple at a potential consistent with the first reduction of 1 (Figure 3b), thus indicating that a de-threading process had occurred. The formation of 1 was confirmed by MALDI-MS and NMR analyses (Figure S12 in the Supporting Information) of the redox cycled solution following removal of electrolyte present in the electrochemical experiment. Thus, upon reduction, 3 begins a de-threading process. It is postulated



FULL PAPER

Figure 3. a) Cyclic voltammograms for **1**, **2** and **3**. All cyclic voltammograms were recorded at ambient temperature in CH_2Cl_2 containing $[Bu_4N][BF_4]$ (0.4 M); b) Cyclic voltammograms of **3** before bulk electrolysis (solid line) and after re-oxidation (dotted line) in CH_2Cl_2 containing $[Bu_4N][BF_4]$ (0.4 M) at 273 K.

that the reduced recognition site of **3** is an unfavourable binding site and repels the electron-rich macrocycle **2**.

To determine the nature of fully reduced 3, both 1, acting as the reference compound, and 3 were monitored by in situ UV/Vis spectroelectrochemistry at an optically transparent electrode. The results for 1 were consistent with previous studies of PTCDI-based species and demonstrated the highly characteristic profiles associated with mono- and dianions (Figure S13-S15 and Table S2 in the Supporting Information).^[15] For **3**, at 273 K exhaustive reduction showed the initial development of bands associated with a monoanionic PTCDI which depleted slowly as electrolysis progressed and were replaced by new bands characteristic of direduction of the PTCDI core, thus confirming the formation of a 3^{2-} species (Figure S16 in the Supporting Information). Re-oxidation of 3^{2-} at this temperature failed to generate the exact spectral profile of 3 (Figure S17 in the Supporting Information) and new bands, in positions consistent with 1

www.chemeurj.org

- 14749

were noted, thereby confirming the results of the bulk electrolysis/CV experiment and indicating the limited de-threading of **3** upon reduction. Repeating the experiment at 230 K (Figure S18 in the Supporting Information) allowed the stabilisation of reduced **3** to at least the **3**⁻ state (slight over-reduction to **3**²⁻ could also be reversed but full reduction to **3**²⁻ was not pursued). Reduction of **3** resulted in the major absorption band shifting to lower energy but a broad feature centred at 530 nm was retained. The latter feature was assigned to a charge transfer band resulting from macrocyclic complexation, thus implying that the [2]-rotaxane is intact upon a one-electron reduction under these conditions.

Complementary to the low temperature NMR studies for 3, evidence for the influence of the macrocycle on the axle in 3⁻ was noted using EPR spectroscopy. The electrochemical one-electron reduction of 1 and 3 produced paramagnetic species consistent with the generation of radical anions. Hyperfine splitting was observed for 1^- which could be simulated as the coupling of the unpaired electron to the nuclei of two nitrogen atoms and three sets of four hydrogen atoms (Figure 4). These may be accounted for by the two sets of four equivalent hydrogen atoms (H_a and H_b) on the perylene core $(a_{4H} = 0.56 \times 10^{-4} \text{ cm}^{-1} \text{ and } 1.68 \times 10^{-4} \text{ cm}^{-1}, \text{ re-}$ spectively) and the four hydrogen atoms at the α -carbon of the imide groups $(a_{4H}=0.13 \times 10^{-4} \text{ cm}^{-1})$. The g_{iso} of 2.0033 was consistent with literature values for a PTCDI anion.^[14] The ambient temperature EPR spectrum of 3^- was similar to that of 1^- in respect to position (g_{iso} of 2.0034 for 3^-) and spectral width (ca. 13 G), thus suggesting that a radical anion based on the PTCDI is present, but differed in spectral shape. Attempts to reproduce all features in the experimental spectrum of 3^- by simulation were unsuccessful. This



Figure 4. a) Experimental EPR spectrum of $\mathbf{1}^{-}$ (bold black line) and simulation (grey line) using $g_{\rm iso} = 2.0033$; $a_{\rm 4H} = 1.68$, 0.56 and 0.13×10^{-4} cm⁻¹ and $a_{\rm 2N} = 0.53 \times 10^{-4}$ cm⁻¹ and a Lorentzian lineshape with a linewidth of 0.12 G. b) Experimental EPR spectrum of $\mathbf{3}^{-}$ (bold black line) and simulation (grey line) using $g_{\rm iso} = 2.0034$; $a_{\rm 4H} = 1.46$, 0.79 and 0.16×10^{-4} cm⁻¹ and a Gaussian lineshape with a linewidth of 0.18 G.

may not be surprising given that reduced **3** shows some instability with respect to de-threading under these conditions (see above), and it was noted that the spectrum appeared to lose some resolution with time. The spectral shape was best reproduced from parameters obtained by converging values assigned to the two largest hyperfine couplings used in the simulation of the EPR spectrum of **1**⁻ (H_a and H_b) whilst maintaining similar couplings for two equivalent nitrogen atoms and the four hydrogen atoms assigned as the α carbon of the imide groups (Figure 4). This result may imply a more even distribution of the electron density about the PTCDI core and confirms the influence of the macrocycle in the reduced form of **3**.

Conclusion

In conclusion, we have successfully synthesised and characterised a perylene diimide based [2]-rotaxane that represents the first example of such a species. The PTCDI moiety successfully acts as a recognition site for complexation of a naphthyl-based macrocyclic species. Importantly, the properties of the PTCDI group are modified by complexation, including the nature of the redox processes. One-electron reduction of 3 leads to the formation of 3^- , a radical anion based [2]-rotaxane, representing a switchable state of the PTCDI based [2]-rotaxane. The second reduction of 3 initiates a de-threading process in the [2]-rotaxane, presumably as a result of electrostatic repulsion of the electron-rich macrocycle from the reduced PTCDI recognition site. This observation, in addition to the synthetic strategies employed in this study, confirms the potential of PTCDI-based rotaxanes as viable targets for the preparation of more complex interlocked species including molecular machines.

Experimental Section

Details of and information relating to further synthetic procedures are given in the Supporting Information. Macrocycle **2** was prepared by a literature method.^[12] All reactions were carried out under an atmosphere of dinitrogen or argon as noted below. Column chromatography was performed on silica gel (Merck silica gel 60, 0.2–0.5 mm, 50–130 mesh). ¹H NMR spectra were measured using a Bruker DPX 400 MHz spectrometer unless otherwise stated. Microanalyses were performed by Stephen Boyer, London Metropolitan University, London, UK. MS spectra (MALDI-TOF-MS) were determined on Voyager-DE-STR mass spectrometer.

Synthesis of 3: Compound **1** (41.7 mg, 0.030 mmol, 1 equiv), **2** (95 mg, 0.149 mmol, 5 equiv) and LiBr (10.3 mg, 0.149 mmol, 5 equiv) were dissolved in CHCl₃/MeOH (95:5, 1.5 mL) and heated to 70 °C for 14 days in a sealed pressure tube. Solvent was removed in vacuo and the dark red residue purified by column chromatography (SiO₂: gradient elution, CHCl₃ to 0.1% MeOH in CHCl₃) to yield the title compound. R_f =0.2, (0.1% MeOH in CHCl₃) as a purple solid (4.9 mg, 0.0024 mmol, 8%); ¹H NMR (400 MHz, CD₂Cl₂): δ =8.47 (s, 8H) 7.31 (d, *J*=8.28 Hz, 2H) 7.17-7.26 (m, 10H) 7.13 (d, *J*=8.66 Hz, 10H) 7.03-7.09 (m, 6H) 6.99 (d, *J*=9.03 Hz, 4H) 6.72 (d, *J*=8.41 Hz, 4H) 6.14 (td, *J*=7.90, 5.10 Hz, 4H) 5.64 (dd, *J*=7.53, 4.27 Hz, 4H) 4.71 (t, *J*=6.30, 4H) 4.49 (t, *J*=5.60, 4H) 4.03 (brd, *J*=15.12, 4.58 Hz, 16H) 3.88 (brd., 8H) 3.74 (brd, *J*=

3.89 Hz, 8H) 2.61 (q, J=7.53 Hz, 4H) 1.29 (s, 32H) 1.22 ppm (t, J=7.59 Hz, 6H); ¹³C NMR (126 MHz, CDCl₃): δ =164.12, 156.97, 156.58, 152.70, 148.75, 148.24, 144.51, 144.32, 144.07, 141.87, 141.34, 141.14, 139.97, 139.03, 134.65, 134.60, 132.31, 131.01, 130.85, 130.65, 129.28, 128.92, 128.63, 128.02, 127.27, 126.61, 125.16, 125.03, 124.71, 124.03, 123.80, 123.10, 121.69, 114.62, 114.43, 114.05, 113.52, 113.11, 105.67, 103.04, 71.51, 71.39, 71.20, 71.02, 70.79, 70.67, 70.55, 70.07, 69.84, 67.93, 67.61, 64.84, 63.11, 55.63, 53.42, 43.57, 39.27, 34.67, 34.33, 34.23, 31.93, 31.59, 31.37, 31.32, 30.32, 29.70, 29.36, 29.06, 28.18, 25.28, 22.66, 22.11, 15.24, 14.12, 11.43 ppm; HRMS (MALDI): m/z calcd for C₁₃₄H₁₃₈N₂O₁₆: 2031.00 [M]; found: 2031.43.

Rotaxane 3 via melt phase: Compound **1** (25 mg, 0.018 mmol, 1 equiv) and macrocycle **2** (58 mg, 0.091 mmol, 5 equiv) were heated to $160 \,^{\circ}$ C for 6 h under N₂. The reaction mixture was extracted with the minimum CHCl₃ and **2** was recovered by recrystallisation from CHCl₃/Et₂O. The ethereal filtrate was concentrated in vacuo and the resultant red residue purified by column chromatography (SiO₂: gradient elution 0.1% MeOH in CHCl₃ to 0.35% MeOH in CHCl₃) to yield **3** as a purple solid (3 mg, 0.0015 mmol, 8%). Spectroscopic data were identical to that of the previous synthetic method, see above.

Single crystal X-ray diffraction data: A purple single crystal of 3 was successfully grown by layering MeOH onto a solution of the compound in toluene. Single crystal X-ray diffraction data for 3 was collected at 120(2) K on Beamline I19 at Diamond Light Source. The crystal structure was solved by dual space methods and refined by difference Fourier techniques^[16] and using the OLEX2 software package.^[17] Hydrogen atoms were placed in calculated positions and refined using a riding model; methyl groups were refined as rigid rotors. Rigid bond and similarity restraints were applied to the displacement parameters of all atoms. Badly disordered solvent molecules could not be modelled and the solvent contribution to the structure factors was removed using PLATON SQUEEZE.^[18] This solvent contribution was calculated to be equivalent to 133 electrons, roughly equivalent to three toluene molecules. Crystal data for 3: C₉₈H₉₄N₂O₆·C₃₆H₄₄O₁₀, M=2266.79, triclinic, space group P-1, a = 12.3285(18) Å, b = 13.103(2) Å, c = 20.068(3) Å, a = 75.090(13), $\beta =$ 78.565(13), $\gamma = 89.624(12)^{\circ}, V = 3067.0(8)$ Å³, Z=1, T=120(2) K, F₀₀₀= 1210, $\rho = 1.227 \text{ g cm}^{-3}$, $\mu = 0.078 \text{ mm}^{-1}$, 41004 reflections measured, 10935 unique ($R_{int} = 0.161$) which were used in all calculations. Final $R_1 = 0.133$, $wR_2 = 0.386$, Goof = 0.98, maximum ΔF peak 0.68 $e\text{Å}^{-3}$. CCDC-843319 (3) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We thank the EPSRC and the University of Nottingham for support and funding, and Diamond Light Source for the award of access to Beamline 119. N.R.C. gratefully acknowledges receipt of a Royal Society Wolfson Merit Award.

- a) J. P. Mathias, J. F. Stoddart, Chem. Soc. Rev. 1992, 21, 215-225;
 b) M. S. Vickers, P. D. Beer, Chem. Soc. Rev. 2007, 36, 211-225;
 c) J. P. Sauvage, Chem. Commun. 2005, 12, 1507-1510;
 d) T. J. Hubin, D. H. Busch, Coord. Chem. Rev. 2000, 200, 5-52;
 e) J. F. Stoddart, Chem. Soc. Rev. 2009, 38, 1802-1820.
- [2] a) V. Balzani, A. Credi, M. Venturi, *Chem. Soc. Rev.* 2009, *38*, 1542–1550; b) S. Saha, J. F. Stoddart, *Chem. Soc. Rev.* 2007, *36*, 77–92; c) W. R. Browne, B. L. Feringa, *Nat. Nanotechnol.* 2006, *1*, 25–35; d) H. Tian, Q. C. Wang, *Chem. Soc. Rev.* 2006, *35*, 361–374; e) M.

-FULL PAPER

Gomez Lopez, J. A. Preece, J. F. Stoddart, *Nanotechnology* **1996**, 7, 183–192; f) J. D. Crowley, S. M. Goldup, A-L. Lee, D. A. Leigh, R. T. McBurney, *Chem. Soc. Rev.* **2009**, *38*, 1530–1541.

- [3] a) H.-R. Tseng, S. A. Vignon, J. F. Stoddart, Angew. Chem. 2003, 115, 1529–1533; Angew. Chem. Int. Ed. 2003, 42, 1491–1495; b) A. Altieri, F. G. Gatti, E. R. Kay, D. A. Leigh, D. Martel, F. Paolucci, A. M. Z. Slawin, J. K. Y. Wong, J. Am. Chem. Soc. 2003, 125, 8644–8654; c) C. P. Collier, G. Mattersteig, E. W. Wong, Y. Luo, K. Beverly, J. Sampaio, F. M. Raymo, J. F. Stoddart, J. R. Heath, Science 2000, 289, 1172–1175.
- [4] a) V. Balzani, A. Credi, S. Silvi, M. Venturi, *Chem. Soc. Rev.* 2006, 35, 1135–1149; b) V. Balzani, M. Clemente-Leo'n, A. Credi, B. Ferrer, M. Venturi, A. H. Flood, J. F. Stoddart, *Proc. Natl. Acad. Sci. USA* 2006, 103, 1178; c) M. R. Panman, P. Bodis, D. J. Shaw, B. H. Bakker, A. C. Newton, E. R. Kay, A. M. Brouwer, W. J. Buma, D. A. Leigh, S. Woutersen, *Science* 2010, 328, 1255–1258.
- [5] a) D. G. Hamilton, L. Prodi, N. Feeder, J. K. M. Sanders, J. Chem. Soc. Perkin Trans. 1 1999, 1057–1066; b) G. Kaiser, T. Jarrosson, S. Otto, Y.-F. Ng, A. D. Bond, J. K. M. Sanders, Angew. Chem. 2004, 116, 1993; Angew. Chem. Int. Ed. 2004, 43, 1959–1962; c) S. A. Vignon, T. Jarrosson, T. Iijima, H. R. Tseng, J. K. M. Sanders, J. F. Stoddart, J. Am. Chem. Soc. 2004, 126, 9884–9885; d) K. D. Johnstone, N. Bampos, J. K. M. Sanders, M. J. Gunter, New J. Chem. 2006, 30, 861–867.
- [6] F. Würthner, Chem. Commun. 2004, 1564-1579.
- [7] Y. Li, H. Li, Y. Li, H. Liu, S. Wang, X. He, N. Wang, D. Zhu, Org. Lett. 2005, 7, 4835–4838.
- [8] J. Baggerman, D. C. Jagesar, R. A. L. Vallée, J. Hofkens, F. C. De Schryver, F. Schelhase, F. Vögtle, A. M. Brouwer, *Chem. Eur. J.* 2007, *13*, 1291–1299.
- [9] P. R. Ashton, M. Bělohhradský, D. Philp, J. F. Stoddart, J. Chem. Soc. Chem. Commun. 1993, 16, 1269–1274.
- [10] a) M. Zorn, S. A. L. Weber, M. N. Tahir, . W. Tremel, H.-J. Butt, R. Berger, R. Zentel, *Nano Lett.* **2010**, *10*, 2812–2816; b) Y. Nagao, *Prog. Org. Coatings* **1997**, *31*, 43–49c) B. A. Jones, A. Facchetti, M. R. Wasielewski, T. J. Marks, *J. Am. Chem. Soc.* **2007**, *129*, 15259–15278.
- [11] T. Iijima, S. A. Vignon, H.-R. Tseng, T. Jarrosson, J. K. M. Sanders, F. Marchioni, M. Venturi, E. Apostoli, V. Balzani, J. F. Stoddart, *Chem. Eur. J.* 2004, *10*, 6375–6392.
- [12] D. G. Hamilton, J. E. Davies, L. Prodi, J. K. M. Sanders, *Chem. Eur. J.* **1998**, *4*, 608–620.
- [13] P. L. Anelli, P. R. Ashton, N. Spencer, A. M. Z. Slawin, J. F. Stoddart, D. J. Williams, *Angew. Chem.* **1991**, *103*, 1052–1054; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1036–1039.
- [14] a) T. W. Chamberlain, E. S. Davies, A. N. Khlobystov, N. R. Champness, *Chem. Eur. J.* 2011, *17*, 3759–3767; b) G. Goretzki, E. S. Davies, S. P. Argent, J. E. Warren, A. J. Blake, N. R. Champness, *Inorg. Chem.* 2009, *48*, 10264–10274; c) G. Goretzki, E. S. Davies, S. P. Argent, W. Alsindi, A. J. Blake, J. E. Warren, J. McMaster, N. R. Champness, *J. Org. Chem.* 2008, *73*, 8808–8814.
- [15] S.-G. Chen, H. M. Branz, S. S. Eaton, P. C. Taylor, R. A. Cormier, B. A. Gregg, J. Phys. Chem. B 2004, 108, 17329–17336.
- [16] G. M. Sheldrick, Acta Crystallogr. Sect. A 2008, 64, 112-122.
- [17] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, J. Appl. Crystallogr. 2009, 42, 339–341.
- [18] a) A. L. Spek, J. Appl. Crystallogr. 2003, 36, 7–13; b) P. v. d. Sluis,
 A. L. Spek, Acta Crystallogr. Sect. A 1990, 46, 194–201.

Received: October 3, 2011 Published online: December 1, 2011