Energy transfer in chiral co-assemblies of triple hydrogen-bonded oligo(*p*-phenylene vinylene)s and porphyrin†

Freek J. M. Hoeben, Maarten J. Pouderoijen, Albertus P. H. J. Schenning* and E. W. Meijer*

Received 4th September 2006, Accepted 13th October 2006
First published as an Advance Article on the web 2nd November 2006
DOI: 10.1039/b612790h

π–π Stacking of hydrogen-bonded porphyrin and oligo(*p*-phenylene vinylene)s (OPVs) yields helical co-assemblies which exhibit energy transfer from OPV to porphyrin.

Self-organisation and molecular recognition based on hydrogen bonding are widely observed phenomena in natural systems, illustrating the strength of hydrogen bonding on directional and cooperative self-assembly.[1] Numerous heterocomplementary hydrogen bonding motifs have been designed; a classic example being the combination of either barbituric or cyanuric acid and melamine *via* triple hydrogen bonding. Originally described in detail by Whitesides *et al.*,[2] the powerful combination of synthetic accessibility and directionality has induced extensive studies aiming at regular patterning of molecular building blocks.[3] Its wide applicability is illustrated by implementation in varying fields including *e.g.* covalent casting,[4] supramolecular networks,[5] electro-optic thin films,[6] gels,[7] double rosette assemblies[8] and supramolecular catalysis.[9] The use of similar, complementary hydrogen bonding interactions for creating functional, π-conjugated assemblies has proven to be an attractive strategy,[10] however, requires a thorough molecular design. Energy or electron transfer studies using hydrogen-bonded dyes are ubiquitous but the molecular components are generally not programmed to self-assemble into elongated, stacked architectures.[11]

We have previously studied self-organisation of hexameric hydrogen-bonded cycles into tubular assemblies in apolar solvent, based on oligo(*p*-phenylene vinylene) derivatives equipped with *s*-triazine units (OPVnTs).[12] Mixed assemblies were obtained by addition of perylene bisimide, bearing a triple hydrogen bonding array complementary to OPVnT.[10] The hydrogen-bonding motif of perylene bisimide resembles that of cyanuric acid and self-assembly of naphthalene bisimides[13a] and perylene bisimides[13b] has indeed been achieved by complementary hydrogen bonding to melamine.

The present paper focuses on stacked co-assemblies displaying energy transfer[14] to an incorporated acceptor moiety bearing a cyanuric acid motif (Chart 1).[15] Cyanuric acid is in principle easily functionalized with any chromophore, rendering this approach widely applicable. A porphyrin derivative bearing enantiomerically pure 3,7-dimethyloctyloxy sidechains was equipped with cyanuric acid (**CN-Por**), resulting in two available sites for hydrogen bonding to OPVnT. **CN-1** and **CN-2** bearing dodecyl tails were synthesized for reference purposes.

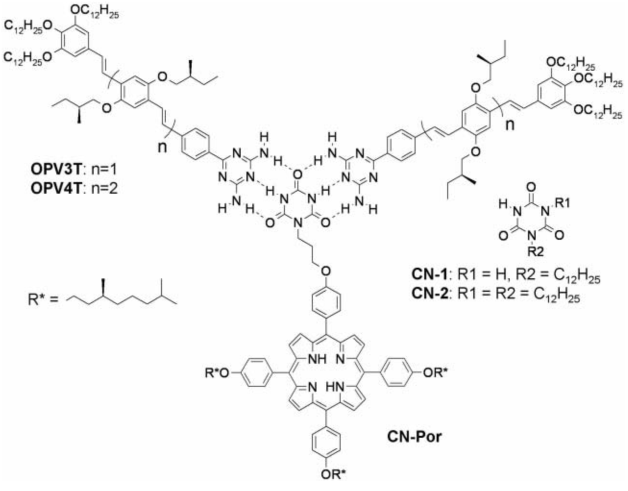

Chart 1

To prove 1 : 2 complexation, **CN-Por** was titrated to molecularly dissolved **OPV4T**. Since the association constant for triple hydrogen bonding in chloroform is low ($K_{\text{ass}} \approx 200\ \text{M}^{-1}$),[16] additional π–π stacking interactions were required to prove 1 : 2 complexation. Therefore, the experiment was performed in methylcyclohexane (MCH, [**OPV4T**] = 2×10^{-5} M), an apolar solvent used previously to induce OPV self-assembly. Upon addition of **CN-Por**, quenching of **OPV4T** fluorescence, caused by both aggregation as well as energy transfer to the porphyrin (*vide infra*), clearly indicated the formation of a 1 : 2 stoichiometric assembly (Fig. 1). It must be stressed that at the relatively low concentrations used, pure **OPV4T** is not self-assembled, as was concluded from concentration-dependent optical studies (Fig. 2).

Having established the intermolecular binding ratio, stoichiometric 1 : 2 **CN-Por**–OPVnT ($n = 1,2$)[18] complexes were subjected to temperature-dependent UV–vis, CD and fluorescence measurements in MCH (Fig. 3 for **OPV4T**).[19] At low temperatures, **OPV4T** and **CN-Por** display highly broadened spectral UV–vis signatures, represented by a red-shifted band at the onset of **OPV4T** absorption at $\lambda = 487$ nm and a broad, diminished porphyrin Soret band. The presence of assembled species is corroborated by a Cotton effect which appears to contain contributions from both chromophores.[20] In the assembled state, the UV–vis spectrum is a summation of the self-assembled spectra found for pure **CN-Por**† and pure **OPV4T**[12] (at elevated concentrations) and OPV fluorescence is almost completely quenched in favor of porphyrin luminescence. This suggests co-assembly of porphyrin

---

Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600, MB Eindhoven, The Netherlands. E-mail: a.p.h.j.schenning@tue.nl, e.w.meijer@tue.nl; Fax: +31 040 245 1036

† Electronic supplementary information (ESI) available: Synthetic procedures, product characterisation and additional optical studies. See DOI: 10.1039/b612790h

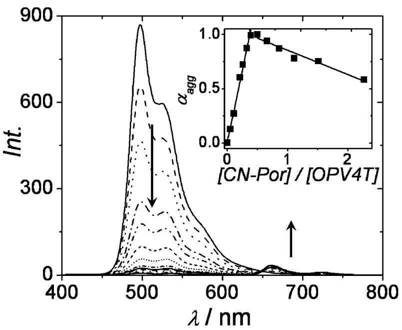

Fig. 1 Fluorescence spectra (λ_{exc} = 340 nm)[17] for the addition of up to 4.5×10^{-5} M **CN-Por** to **OPV4T** (constant at 2×10^{-5} M) in MCH. The inset shows the fraction of aggregated species, determined by plotting the ratio of luminescence intensities at λ = 497 nm and λ = 527 nm, as a function of **CN-Por** addition.

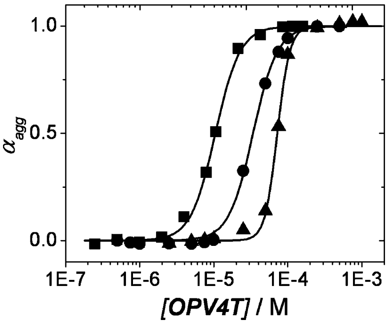

Fig. 2 Self-assembly of **OPV4T** (▲) and of its 1 : 2 hydrogen-bonded complexes with **CN-1** (●) and **CN-Por** (■), based on concentration-dependent fluorescence data. Lines to guide the eye.

and OPVnT into separate, hydrogen-bonded stacks[21] displaying energy transfer from the OPVs to the porphyrin moiety. Moreover, since porphyrin absorption at λ_{exc} = 340 nm does not change significantly with temperature,† a considerable antenna effect is observed in the co-assemblies, as evidenced by the significant increase of porphyrin luminescence.

At high temperature, the spectral features indicate disassembly of the system characterised by molecularly dissolved absorption features, the loss of the Cotton effect and recovery of OPV fluorescence. This fully reversible transition from co-aggregates to molecularly dissolved species occurs at a transition temperature of 48 °C using **OPV4T** (4×10^{-5} M) and, surprisingly, showed no significant dependence on conjugation length.[22]

Stoichiometric 1 : 2 **CN-1**–OPVnT (n = 1,2)[18] complexes were also subjected to temperature-dependent optical measurements in MCH to probe the influence of the cyanuric acid moiety on co-assembly.† At low temperature, the absorption maximum of **OPV4T** exhibits a relatively large bathochromic shift from λ = 427 nm to λ = 443 nm and concomitantly, **OPV4T** luminescence is strongly quenched and red-shifted. Moreover, the chirality of the (*S*)-methylbutyloxy sidechains is expressed at the supramolecular level in a bisignate Cotton effect with a zero-crossing at λ = 448 nm, close to the absorption maximum at low temperatures. All observed spectral changes are fully reversible and the transition temperature is 33 °C for **OPV4T** (4×10^{-5} M), again showing no dependence on conjugation length. From these overall results it can be concluded that both OPVnTs form 1 : 2 helical co-assemblies with cyanuric acid. For both oligomers, the observed transition temperature is higher in hydrogen-bonded co-assemblies with **CN-Por** then with **CN-1**, presumably as a consequence of additional porphyrin stacking interactions. The clear absence of a significant stability dependence on OPV conjugation length is in sharp contrast with previously studied systems,[10,12,22] suggesting that in the specific assembly geometry the OPVs have a diminished influence on the stacking behavior.

Apparently, hydrogen bonding to cyanuric acid provides a scaffold for aggregation *via* stacking of the π-conjugated backbones. Since both pure OPVnTs are not aggregated at 4×10^{-5} M and a 1 : 1 **CN-2**–**OPV4T** complex did not show any signs of aggregation,† increased π–π interactions are required for assembly at this concentration. This hypothesis was further enhanced by concentration-dependent measurements on **OPV4T** and 1 : 2 complexes of **CN-1**–**OPV4T** and **CN-Por**–**OPV4T** (Fig. 2). Assembly of both hydrogen-bonded complexes occurs at a lower concentration as compared to pure **OPV4T**. Moreover, aggregation of the complex with **CN-Por** is stabilized with respect to **CN-1** as a consequence of additional π–π stacking interactions of the porphyrin moiety. These findings confirm the increased transition temperature upon going from a **CN-1** to a **CN-Por** co-assembly.

In the co-assembled state, **CN-Por** is expected to act as an energy acceptor from OPV.[23] When comparing the previous experiments, the fluorescence of both OPVnTs is much more quenched in co-assemblies with **CN-Por** than with **CN-1**. This effect seems to be stronger for **OPV4T** than for **OPV3T**, which may be a consequence of the more red-shifted fluorescence of **OPV4T**, allowing for a better spectral overlap between OPV fluorescence and the Q-bands of **CN-Por**.[24] To probe energy

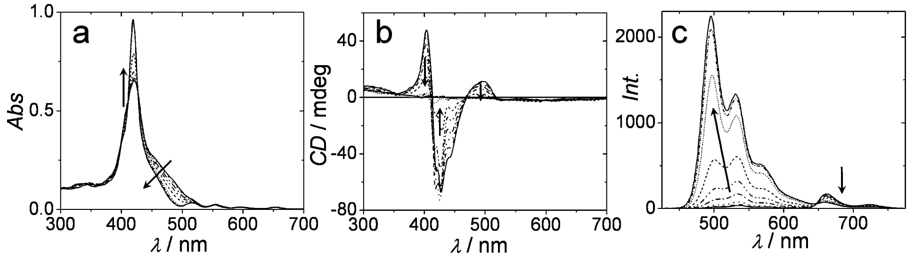

Fig. 3 Temperature-dependent (a) UV–vis (b) CD and (c) fluorescence (λ_{exc} = 340 nm) studies on 1 : 2 **CN-Por**–**OPV4T** ([**OPV4T**] = 4×10^{-5} M) in MCH. The arrows indicate a temperature increase from 0 °C to 80 °C.

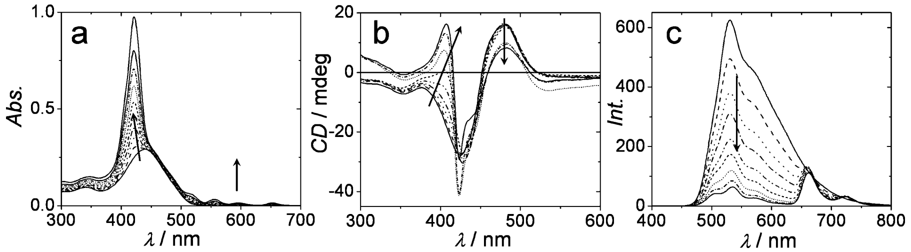

Fig. 4 Exchange experiments performed by the addition of 0 to 40 mol% **CN-Por** to co-assembled **CN-1**–**OPV4T** in MCH at room temperature monitored with (a) UV–vis (b) CD and (c) fluorescence ($\lambda_{exc} = 340$ nm) spectroscopy ([**OPV4T**] = constant at 4×10^{-5} M).

transfer from **OPV4T** to the porphyrin, an exchange experiment was performed starting from a 1 : 2 **CN-1**–**OPV4T** co-assembly in MCH (Fig. 4, $\lambda_{exc} = 340$ nm). Upon increasing the **CN-Por** content from 0 to 40 mol% (compared to **OPV4T**),[25] the characteristic self-assembled **OPV4T** fluorescence with its principal peak at $\lambda_{em} = 530$ nm decreases in intensity in favour of porphyrin luminescence at $\lambda_{em} = 660$ nm and $\lambda_{em} = 724$ nm, indicative of energy transfer from **OPV4T** to the porphyrin moiety. The initial decrease follows Stern–Volmer behaviour ($K_{SV} = 3.0 \times 10^5$ M^{-1}) with a positive deviation from linearity at higher **CN-Por** concentrations.† Concomitantly, the UV–vis and CD spectra show a gradual transition from a pure 1 : 2 **CN-1**–**OPV4T** assembly to a mixed OPV–porphyrin assembled system. At the point where a 1 : 2 **CN-Por**–**OPV4T** stoichiometry is reached, the **OPV4T** fluorescence quenching is similar to that observed in Fig. 3. The enhanced stability of co-assembled **OPV4T**–**CN-Por** apparently ensures the complete exchange of **CN-1** for **CN-Por**.

In conclusion, we have made use of the classical melamine-cyanuric acid hydrogen-bonding couple for the formation of helically ordered, π-conjugated co-assemblies in dilute solution. Non-covalent incorporation of an energy acceptor, thus imparting functionality to these architectures, may prove valuable in the quest for the successful implementation of supramolecular electronics.

Acknowledgements

The authors acknowledge financial support from the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (CW-NWO).

References

1 D. S. Lawrence, T. Jiang and M. Levett, *Chem. Rev.*, 1995, **95**, 2229–2260, and references therein.
2 (*a*) J. A. Zerkowski, C. T. Seto and G. M. Whitesides, *J. Am. Chem. Soc.*, 1992, **114**, 5473–5475; (*b*) G. M. Whitesides, E. E. Simanek, J. P. Mathias, C. T. Seto, D. N. Chin, M. Mammen and D. M. Gordon, *Acc. Chem. Res.*, 1995, **28**, 37–44.
3 M. Mascal, J. Hansen, P. S. Fallon, A. J. Blake, B. R. Heywood, M. H. Moore and J. P. Turkenburg, *Chem.–Eur. J.*, 1999, **5**, 381–384.
4 E. E. Archer, A. E. Sochia and M. J. Krische, *Chem.–Eur. J.*, 2001, **7**, 2059–2065.
5 H. Koyano, P. Bissel, K. Yoshihara, K. Ariga and T. Kunitake, *Langmuir*, 1997, **13**, 5426–5432.
6 (*a*) P. Zhu, H. Kang, A. Facchetti, G. Evmenenko, P. Dutta and T. J. Marks, *J. Am. Chem. Soc.*, 2003, **125**, 11496–11497; (*b*) S. Keinan, M. A. Ratner and T. J. Marks, *Chem. Mater.*, 2004, **16**, 1848–1854.
7 (*a*) K. Hanabusa, T. Miki, Y. Tagushi, T. Koyama and H. Shirai, *J. Chem. Soc., Chem. Commun.*, 1993, 1382–1384; (*b*) S. Yagai, M. Higashi, T. Karatsu and A. Kitamura, *Chem. Mater.*, 2004, **16**, 3582–3585.
8 P. Timmerman and L. J. Prins, *Eur. J. Org. Chem.*, 2001, 3191–3205.
9 N. McClenaghan, C. Absalon and D. M. Bassani, *J. Am. Chem. Soc.*, 2003, **125**, 13004–13005.
10 F. Würthner, Z. Chen, F. J. M. Hoeben, P. Osswald, C.-C. You, P. Jonkheijm, J. van Herrikhuyzen, A. P. H. J. Schenning, P. P. A. M. van der Schoot, E. W. Meijer, E. H. A. Beckers, S. C. J. Meskers and R. A. J. Janssen, *J. Am. Chem. Soc.*, 2004, **126**, 10611–10618.
11 (*a*) F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer and A. P. H. J. Schenning, *Chem. Rev.*, 2005, **105**, 1491–1546; (*b*) A. Ajayaghosh, S. J. George and A. P. H. J. Schenning, *Top. Curr. Chem.*, 2005, **258**, 83–118.
12 P. Jonkheijm, A. Miura, M. Zdanowska, F. J. M. Hoeben, S. De Feyter, A. P. H. J. Schenning, F. C. De Schryver and E. W. Meijer, *Angew. Chem., Int. Ed.*, 2004, **43**, 74–78.
13 (*a*) N. Kimizuka, T. Kawasaki, K. Hirata and T. Kunitake, *J. Am. Chem. Soc.*, 1995, **117**, 6360–6361; (*b*) F. Würthner, C. Thalacker and A. Sautter, *Adv. Mater.*, 1999, **11**, 754–758.
14 F. J. M. Hoeben, L. M. Herz, C. Daniel, P. Jonkheijm, A. P. H. J. Schenning, C. Silva, S. C. J. Meskers, D. Beljonne, R. T. Phillips, R. H. Friend and E. W. Meijer, *Angew. Chem., Int. Ed.*, 2004, **43**, 1976–1979.
15 We became aware of a German patent in which porphyrin is equipped with cyanuric acid *via* an ester linkage: T. S. Balaban, J.-M. Lehn, S. Lebedkin and M.-J. Brienne, Forschungszentrum Karlsruhe Gmbh, Germany, DE10146970, 2003.
16 F. Würthner, C. Thalacker, A. Sautter, W. Schärtl, W. Ibach and O. Hollricher, *Chem.–Eur. J.*, 2000, **6**, 3871–3886.
17 In order to excite the OPVs with maximum probability, this wavelength was selected on the basis of the UV–vis spectra of **CN-Por** and OPVnT.
18 Pure **CN-Por** reversibly self-assembles in MCH with a clear transition temperature of 42 °C (2×10^{-5} M).
19 Complexes with **OPV3T** and **OPV4T** have similar properties and optical spectra for the former are given in the supporting information†.
20 The overlapping circular dichroism cannot be explained purely based on exciton theory, since this would counterintuitively imply a right-handed OPV and a left-handed porphyrin stacking.
21 We have not studied the self-assembly mechanism of this system in detail, see: P. Jonkheijm, P. P. A. M. van der Schoot, A. P. H. J. Schenning and E. W. Meijer, *Science*, 2006, **313**, 80–83.
22 P. Jonkheijm, F. J. M. Hoeben, R. Kleppinger, J. van Herrikhuyzen, A. P. H. J. Schenning and E. W. Meijer, *J. Am. Chem. Soc.*, 2003, **125**, 15941–15949.
23 M. Wolffs, F. J. M. Hoeben, E. H. A. Beckers, A. P. H. J. Schenning and E. W. Meijer, *J. Am. Chem. Soc.*, 2005, **127**, 13484–13485.
24 T. Förster, *Discuss. Faraday Soc.*, 1959, **27**, 7–17.
25 Excluding concentration effects, **CN-Por** was dissolved in a portion of the 1 : 2 **CN-1**–**OPV4T** solution which was added to the original 1 : 2 **CN-1**–**OPV4T** solution. Mixtures were heated at 80 °C for 1 min to allow for intimate intermixing.