Tetrahedron 64 (2008) 11480–11489

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Self-assembly of supramolecular oligo-phenylene-ethynylene wires consisting of double Hamilton receptor modified OPE rods and a tetraphenylporphyrin cyanurate

Florian Wessendorf, Andreas Hirsch *

Department of Chemistry and Pharmacy and Interdisciplinary Center for Molecular Materials (ICMM), Friedrich-Alexander Universität Erlangen-Nürnberg, Henkestraße 42, 91054 Erlangen, Germany

ARTICLE INFO

Article history:
Received 5 June 2008
Received in revised form 5 August 2008
Accepted 20 August 2008
Available online 27 August 2008

Keywords:
Oligo-phenylene-ethynylene
Porphyrins
Hamilton receptor
Hydrogen bonding
Self-assembly

ABSTRACT

The syntheses and characterizations of new oligo-phenylene-ethynylene (OPE) bridged bis-Hamilton receptors **8**–**9** and their linear H-bonding behaviour with a new cyanuric acid modified tetraphenylporphyrin (TPP) **13** are reported. The resulting rigid complexes consisting of an oligo-phenylene-acetylene wire and two terminating TPPs were characterized by ^{1}H NMR, UV/vis and fluorescence spectroscopies. The 1:2 compositions of the supramolecular complexes, the association constants K_n and the cooperativity of binding expressed by Scatchard plots and Hill coefficients η_H were determined by ^{1}H NMR titration experiments. The strength of the association constants K_n in $CDCl_3$ at rt was found to be in a range of 10^5 and 10^6 mol^{-1} dm^3 for the first complexation and 10^{10}–10^{12} mol^{-1} dm^3 for the second complexation, which is rather strong.

1. Introduction

Poly- and oligo-conjugated π-systems such as polymeric and oligomeric *p*-phenylenevinylenes (*p*-PPV/*p*-OPV), *p*-phenylenes (*p*-PP/*p*-OP), alkylthiophenes (PAT/OAT) and *p*-phenylene-ethynylenes (*p*-PPE/*p*-OPE) are known for their interesting electronic, photoluminescence and electroluminescence properties.[1] The supramolecular arrangement of π-conjugated systems is a rather new and interesting topic in modern chemistry and nanoscience.[2] Particular linear and rigid chains in the nanometer regime consisting of π-conjugated molecules have fascinating features with respect to their semiconducting behaviour and their possible application as nanowires between electrodes.[3] However, to assure electron tunnelling through supramolecular arrays and to compare these with inorganic wires[4] and carbon nanotubes[5] several aspects have to be taken into account. Purity of the organic monomers is crucial due to possible trapping of holes and electrons by impurities.

We recently have introduced the Hamilton receptor[6a]/cyanuric acid binding motif to self-assemble dendritic architectures (Fig. 1).[6b–e] The six-point hydrogen bonding exhibits comparatively strong binding interaction between host and guest. Association constants K_n that range in apolar solvents (i.e., dichloromethane, chloroform and toluene) from 10^3 to 10^6 M^{-1} could be determined.[6g] Besides achiral and chiral dendritic building blocks such as depsipeptide dendrons we have also introduced chromophoric components for self-assembled architectures, namely, fullereneated cyanuric acid end caps and Hamilton receptor substituted porphyrin cores.[6f] In the case of the Hamilton receptor/cyanuric acid concept the assembled complexes have been proved to be relatively stable at moderate temperature and inert in non-polar solvents like dichloromethane and toluene. Disintegration into the isolated key and lock components of those nanohybrids can only be achieved by adding hydrogen bonding breaking solvents like THF or methanol.

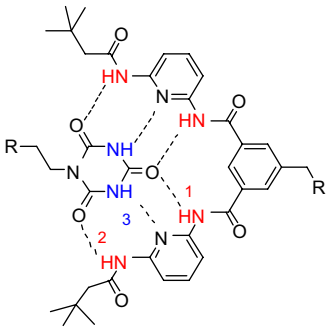


Figure 1. Hamilton receptor cyanuric acid binding motif.

* Corresponding author.
E-mail address: andreas.hirsch@chemie.uni-erlangen.de (A. Hirsch).

0040-4020/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2008.08.054

We now describe three new conjugated supramolecular π-systems consisting of three different *p*-OPEs **7**–**9** and a tetraphenylporphyrin **13** as chromophoric end cap. The *p*-OPEs are terminated with a Hamilton receptor at each end for the complexation with a cyanuric acid bearing tetraphenylporphyrin (TPP). Based on ^{1}H NMR titration experiments we have analyzed the complexation behaviour of the new *p*-OPEs.

2. Results and discussion

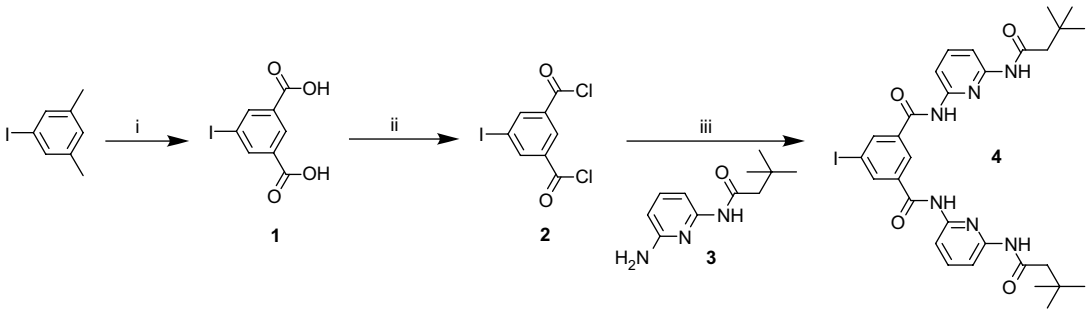
2.1. Synthesis

The target *p*-OPEs were synthesized starting from commercially available 5-iodo-xylene, which can be easily oxidized by $KMnO_4$ to 5-iodo-isophthalic acid **1**. Treatment of the diacid **1** with thionyl chloride ($SOCl_2$) at reflux and under dry conditions led to dichloride **2**, which then could be coupled with aminopyridine derivative **3**[7] affording the iodo-Hamilton receptor **4** in 94% isolated yield (Scheme 1).

Homo coupling of compound **6** led to linear molecule **7**, which contains a butadiyne linker and two Hamilton receptors as end cap. Hamilton receptor derivative **6** could also be coupled under Sonogashira conditions either with 1,4-diiodobenzene or with 1,4-diiodo-2,5-bis(octyloxy)benzene to give the corresponding rod-like derivatives **8** and **9** with OPE character and two Hamilton receptor end caps (Scheme 3).

Cyanuric acid bearing porphyrins are expected to be model compounds for binding with the rod-shaped bis-Hamilton receptors **7**–**9** due to their electron donor properties. Our basic concept was to synthesize a tetraphenylporphyrin (TPP), which has just one cyanuric acid functionality and three additional substituents to provide a sufficient solubility. Therefore 4-trimethylsilylethynylbenzaldehyde and 3,5-dimethoxy benzaldehyde were chosen as starting materials. The synthesis was performed under statistical Lindsey conditions (Scheme 4).[9]

Four equivalents of pyrrole, 1 equiv of 4-trimethylsilylethynylbenzaldehyde and 3 equiv of 3,5-dimethoxy benzaldehyde were dissolved in dichloromethane. Then TFA (trifluoroacetic acid) was

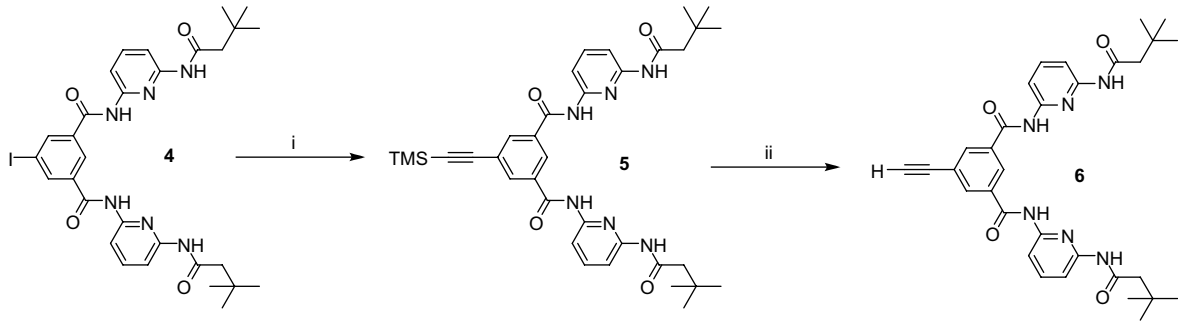


Scheme 1. Synthesis of iodo-Hamilton receptor **5**. (i) $KMnO_4$, *tert*-butanol/H_2O, 1:1, 100 °C, 20 h; (ii) $SOCl_2$, DMF, reflux, 6 h; (iii) NEt_3, THF, 0 °C→rt, 12 h.

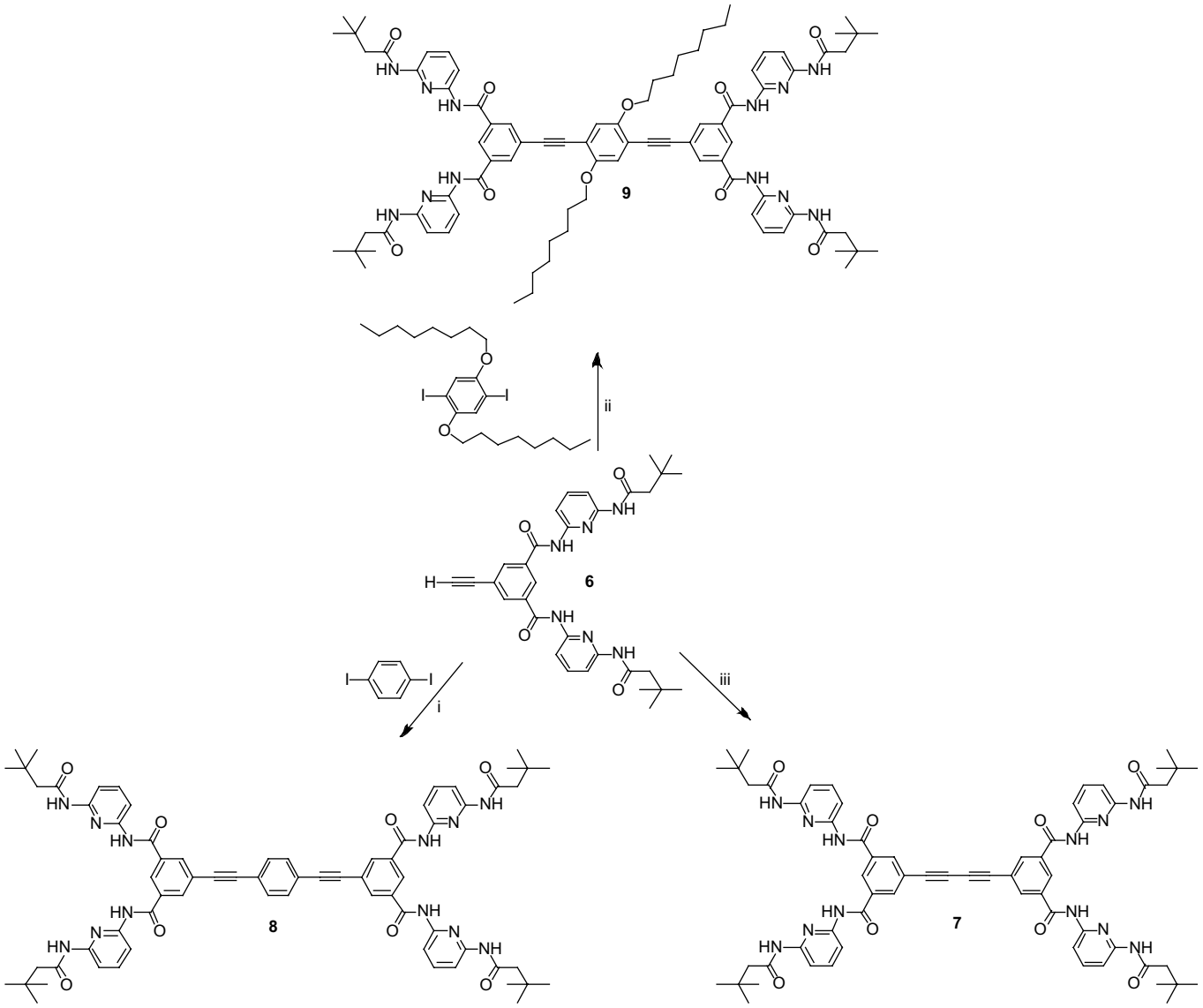
The iodo-compound **4** is a suitable precursor for the synthesis of rod-like carbon chains with a Hamilton receptor as end cap. Therefore various C–C cross coupling techniques are in principle possible. Most promising in this case are Sonogashira coupling techniques[8] with terminal acetylenes. Trimethylsilylacetylene was coupled in nearly quantitative yield at rt with the iodo-Hamilton receptor **4** (Scheme 2). As Pd^0 source, $Pd(PPh_3)_2Cl_2$ was chosen and triphenylphosphine was used as additional ligand. Deprotection of the resulting Hamilton receptor **5** using TBAF (tetrabutyl ammonium fluoride) as fluoride source led to the terminal ethynyl derivative **6**. Important for a good yield and for avoiding dimerization was to keep the temperature at or below 25 °C during the reaction process and the work-up. The obtained terminal acetylene group was then used to elongate the chain or to synthesize linear structures with two Hamilton receptor end caps for H-bonded oligomers and polymers.

added and the solution was stirred for 1 h before NEt_3 was added to neutralize the reaction mixture. The final oxidation was performed with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone). Separation of all statistically formed porphyrin isomers was possible by careful column chromatography (hexanes/EtOAc 4:1). Monosubstituted 4-trimethylsilyl-ethynyl TPP **10** was isolated in 5% yield after precipitating with *n*-pentane. The yield is typical for this type of reaction. Metallation with zinc is straightforward in the case of tetraphenylporphyrins. Zinc porphyrins have been intensively investigated with respect to their photophysical properties and are very attractive building blocks for architectures enabling photoinduced electron transfer.[6f,10] The metallation was carried out in refluxing THF using zinc(II) acetate as zinc(II) source (Scheme 4).

Mild deprotection could be promoted by addition of TBAF to a solution of **11** in THF. Porphyrin **12** was accessible in nearly quantitative yield by this route (Scheme 5). Sonogashira coupling of



Scheme 2. Synthesis of basic Hamilton receptor **6**. (i) Trimethylsilylacetylene, $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, THF, NEt_3, rt, 24 h; (ii) TBAF, THF, rt, 3 h.



Scheme 3. Syntheses of target *p*-OPEs. (i) $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, THF, HN*i*-Pr_2, rt, 60 h; (ii) $Pd(PPh_3)_2Cl_2$, CuI, THF, $HNEt_2$, rt, 72 h; (iii) $Pd(PPh_3)_2Cl_2$, CuI, THF, NEt_3, 70 °C→rt, 52 h.

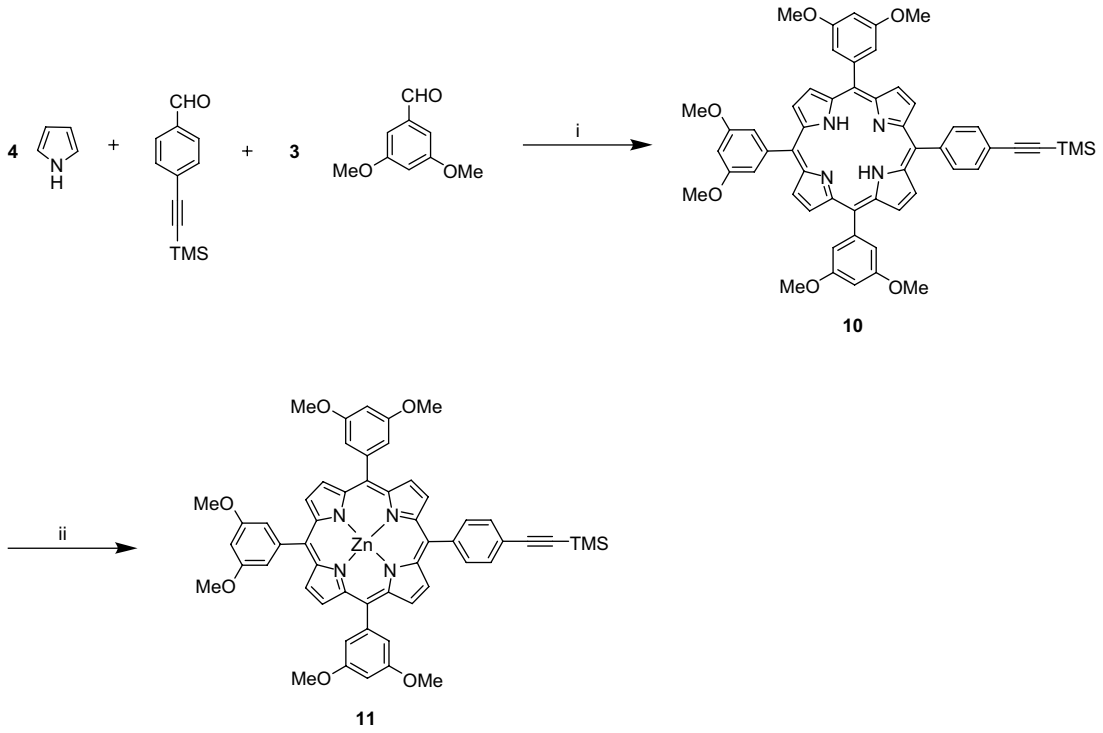
the free acetylenic porphyrin **12** with 4-iodophenyl isocyanuric acid using CuI, Pd_2dba_3 and triphenyl arsine as catalyst ligand systems in a mixture of NEt_3 and THF (Scheme 5) led to the desired cyanuric acid modified porphyrin **13** in good yield (81%). To purify target porphyrin **13** dissolving in THF and precipitation with *n*-pentane was necessary to get rid of solvent inclusion.

2.2. Determination of association constants and cooperativity of binding

The ^{1}H NMR spectra of the Hamilton receptor bearing *p*-OPEs **7**–**9** in $CDCl_3$ show rather broad and poorly resolved signals. This is due to the presence of the large number of hydrogen-bond donors and acceptors causing the formation of intra- and intermolecular bonding networks.[6b,c,g] Pronounced aggregation of **7**–**9** due to intermolecular hydrogen bonds is also the reason for the relatively low solubility of all described *p*-OPEs in chloroform. Using THF or DMSO as hydrogen bond breaking solvents leads to well-resolved NMR spectra of **7**–**9**. In this case, intermolecular associations are not favoured. Remarkable sharpening of the signals in $CDCl_3$ occurs also upon successive addition of the porphyrin cyanuric acid derivative **13**.

The sharpening of the signals is accompanied by a characteristic downfield shift of the amide proton NH1 and NH2 of the bis-Hamilton receptor derivatives and indicates the formation of distinct H-bonding complexes (Fig. 2).[6] The 1:2 binding stoichiometry of the complexes (Scheme 6) was confirmed by applying Job's method of continuous variation to the NMR experiments (Fig. 3).[6b,g] The chemical shift variation of NH1 ($\Delta(\delta)$) as a function of the mole fraction of porphyrin **13** X(13) was monitored and plotted.

A series of ^{1}H NMR titration experiments in $CDCl_3$ were performed in order to determine the association constants and to analyse cooperativity phenomena. Herein, the downfield shifts of the NH1 protons and NH2 protons of the *p*-OPEs were determined as a function of the porphyrin concentration. In a typical titration experiment 0.5 mL of a 3.3 mM solution of a *p*-OPE was titrated with 50 μL of a 10 mM solution of porphyrin **13** for the determination of K_n. It is important to emphasize that the establishment of stable equilibria required some time due to the intermolecular interactions between the free *p*-OPE ligands, which have to be overcome before the binding of the cyanuric acid bearing porphyrin can occur. Consequently, the ^{1}H NMR spectra were taken 30 min after mixing of the components. Notably, a sigmoidal



Scheme 4. Synthesis of zinc porphyrin **11**: i). 1TFA, 60 min; 2. NEt_3, 8 min; 3. DDQ, 15 h; CH_2Cl_2, rt; (ii) $Zn(OAc)_2$, THF, reflux, 4 h.

titration curve can be obtained by plotting the chemical shifts δ of the NH protons as a function of the added porphyrin equivalents (Fig. 4). Such a sigmoidal behaviour is a characteristic feature for positive cooperativity associated with the subsequent binding of guest molecules.[11]

We were then able to calculate the association constants for the binding of the cyanuric acid bearing porphyrin **13** by using the program Chem-Equili.[12] The association constants are summarized in Table 1. The calculations were based on the assumptions of two equilibria (Eqs. 1 and 2) where OPE could be **7**, **8** or **9** and P is cyanuric acid bearing porphyrin **13**.

$$K_1 = \mathrm{OPE} + \mathrm{P} \rightleftharpoons \mathrm{OPE:P} \tag{1}$$

$$K_2 = \mathrm{P} + \mathrm{OPE:P} \rightleftharpoons \mathrm{OPE:P_2} \tag{2}$$

For the case of statistical binding, Eq. 3 must be fulfilled,[11a] for which t is the total number of binding sites (in this case t=2).

$$\frac{K_{n+1}}{K_n} \equiv \frac{n(t-n)}{(n+1)(t-n+1)} \tag{3}$$

However, the experimental values for K_{n+1}/K_n are much higher than those obtained from Eq. 3, which clearly demonstrates the presence of pronounced positive cooperativity.

In other words the free binding energy of the porphyrin increases by going from the monocomplex to the biscomplexes. This is also reflected by the sigmoidal shape of the corresponding titration curves (Fig. 4).

The determination of the occupancy r is certainly one of the most straightforward tools for underlining cooperativity phenomena. The occupancy is the average number of ligands bound to the receptor.[6g]

$$r = \frac{[1\cdot\mathrm{P}] + 2[1\cdot\mathrm{P_2}]}{[1] + [1\cdot\mathrm{P}] + [1\cdot\mathrm{P_2}]} \tag{4}$$

For statistical binding, r can be described by the Scatchard equation 5,[6g] in which Q is the site binding constant and x the concentration of the added ligand.

$$r = \frac{t\cdot Q\cdot x}{1 + Q\cdot x} \tag{5}$$

In the case of statistical binding, the Scatchard plot r/x as a function of r is a straight line. Positive cooperativity exists when the plot is no longer a straight line but a concave curve.

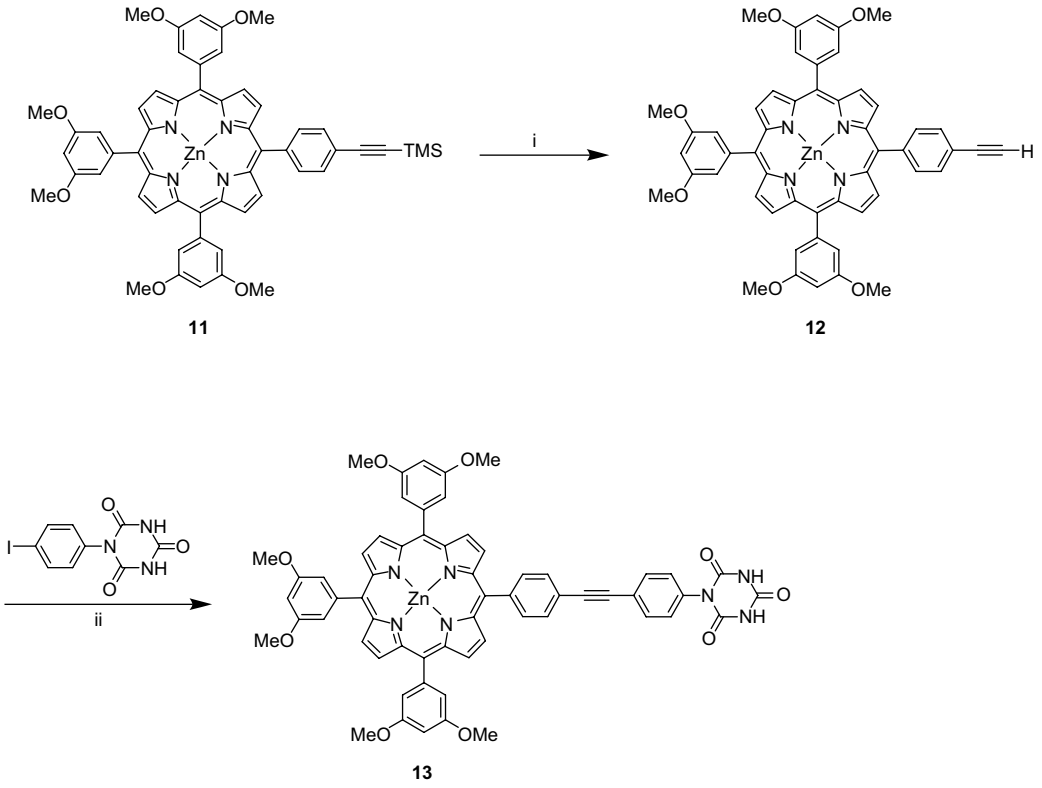
All the Scatchard plots of the titrated *p*-OPE systems display very pronounced concave behaviour (Fig. 5). The amount of cooperativity of a supramolecular system is usually quantified by the Hill coefficient η_H, which can be obtained from the maximum of the Scatchard plot according to Eq. 6.

$$n_H = \frac{r_{max}}{t - r_{max}} \tag{6}$$

The higher the value of η_H, the higher is the degree of cooperativity. For infinitely high cooperativity, η_H becomes equal to t (here t=2). However, this has never been observed in real systems. All Hill coefficients are summarized in Table 1.

The association constants K_n for the first complexation are in the expected range of 10^5–10^6 L mol^{-1}. This is in good agreement with the literature-known Hamilton receptor cyanuric acid complexes.[6] Interestingly the association constants for the second complexation are extremely high (10^{10}–10^{12} L mol^{-1}) compared to much more flexible systems that we already reported.[6b–f] Typical association constants for further complexation of dendritic cyanurates are in the range of 10^3–10^6 L mol^{-1}.[6b–f] Probably the stiffness of the *p*-OPEs in comparison to the more flexible alkyl chains of the literature-known systems is responsible for this trend. Additionally, the significant lower solubility of the free species and the complexes compared to dendritic systems might play another important role.

The decrease of free OPE wire and the formation of the 1:1 and 1:2 complexes during the titration experiments are shown in Figure 6.



Scheme 5. Synthesis of target porphyrin **13**. (i) TBAF, THF, rt, 2 h; (ii) Pd_2dba_3, $AsPh_3$, THF, NEt_3, rt, 3 days.

2.3. UV/vis and fluorescence titration experiments

Electronic communication between the electroactive zinc porphyrin end caps and the inactive bridging *p*-OPEs should be rather unlikely. To prove the absence of electronic interactions between the rod-shaped *p*-OPEs and the cyanuric acid bearing porphyrin we carried out a series of UV/vis and steady-state fluorescence titration experiments. All steady-state fluorescence and absorption measurements were performed in dichloromethane at rt. Importantly, a well-defined concentration of the porphyrin derivatives was needed.

Therefore, 250 μL of a porphyrin stock solution was diluted to a total volume of 1.4 mL as a porphyrin reference. For the following titration steps 50 μL of the *p*-OPE derivative was added to 250 μL of the porphyrin stock solution and filled up to a total volume of 1.4 mL. After each addition step and waiting for 15 min absorption and, fluorescence spectra were recorded. As expected, neither a shift of the SORET band of porphyrin **13** nor a shift of the absorption band of the *p*-OPEs could be detected (Fig. 7).

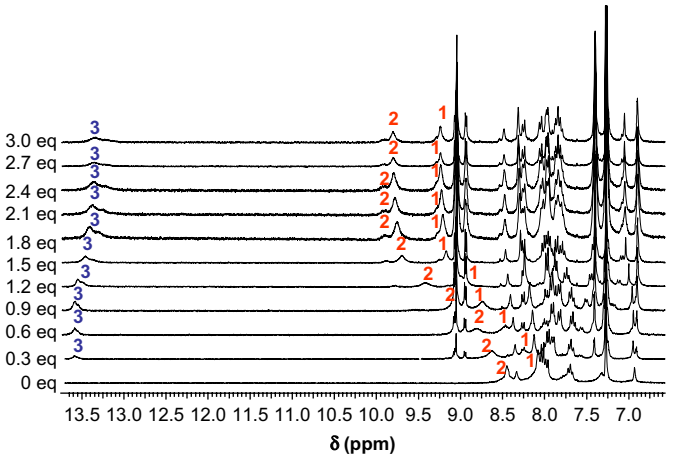


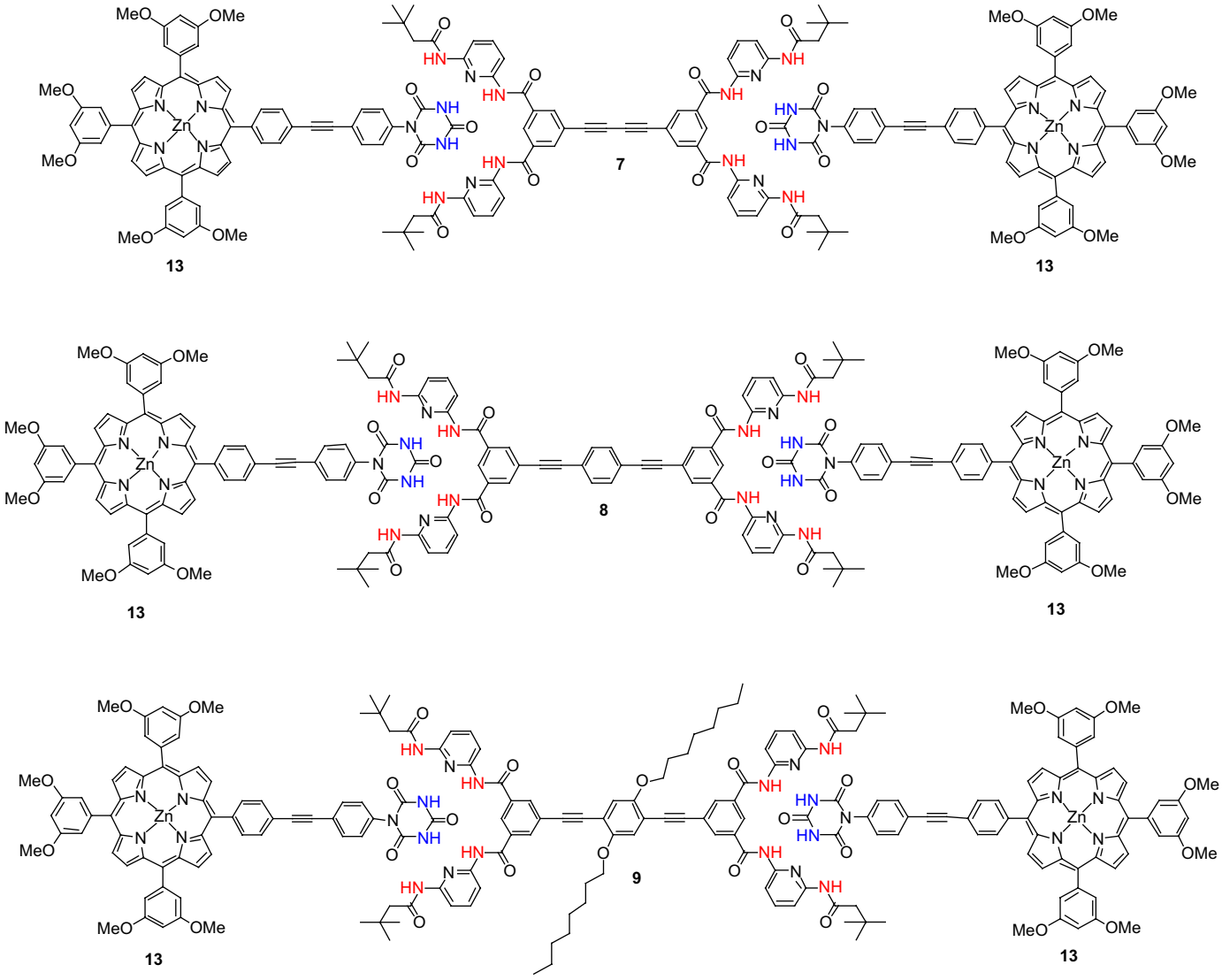
Figure 2. Binding motif between **7**–**9** and **13** with indication of the NH protons NH1, NH2 and NH3 (top) and 300 MHz ^{1}H NMR spectra of **9** at a concentration of 3.3 mM in $CDCl_3$ in the presence of various equivalents of **13** (bottom).

The steady-state fluorescence spectra were measured shortly after recording the absorption spectra. As excitation wavelength the SORET absorption band (422 nm) of the porphyrin **13** was chosen. As is well known from several examples porphyrins might either activate an energy or electron transfer, if they are excited at the SORET band.[6f,10c,13] The emission spectrum of zinc porphyrin **13** shows two emission bands at 598 and 642 nm. A potential electron or energy transfer can be implied, if a decrease of the fluorescence emission intensity is observed. As expected, in all analyzed systems this is not the case (Fig. 8). The experiments prove that the electronic structure of both subunits apparently does not permit a photoinduced electron or energy transfer processes.

Taking the results of the UV/vis and fluorescence titration experiments into account *p*-OPEs can play an interesting and important role as inactive bridges for the supramolecular connection between electron donor–acceptor arrays like porphyrins and fullerenes.

3. Conclusions

We have investigated for the first time the self-assembly of supramolecular rigid *p*-oligo-phenylene-ethynyl-porphyrin donor-wire nanohybrids connected via a Hamilton receptor based hydrogen bonding motif. In this light, we synthesized three different *p*-OPEs carrying two Hamilton receptor termini and a cyanuric acid bearing zinc porphyrin derivative. To improve the relatively poor solubility of the *p*-OPEs in $CDCl_3$ and CH_2Cl_2 we introduced two octyloxy groups at the central benzene core in derivative **9**. The linear aggregation of these building blocks was analyzed by ^{1}H NMR titration experiments. As expected 1:2 complexes were formed, which is proven by Job's plot analysis. The subsequent



Scheme 6. Supramolecular aggregates **7**:**13**$_2$, **8**:**13**$_2$ and **9**:**13**$_2$.

binding of the porphyrin to the *p*-OPE receptors shows an overall positive cooperativity for all cases. Compared to more flexible systems, which contain alkyl chains and bulky groups[6] the association constants K_n associated with twofold binding processes are rather high ($\log K_1$ between 5.00 and 6.40 L mol^{-1}, $\log K_2$ between 10.03 and 12.05 L mol^{-1}). Interestingly the most soluble *p*-OPE system **9** shows the strongest binding constants whereas the cooperativity of the less soluble *p*-OPEs **7** and **8**, expressed by the Hill coefficient η_H, is higher.[14] As expected an electronic communication between both subunits could not be detected by UV/vis and fluorescence experiments.[15]

4. Experimental section

4.1. General remarks

Chemicals. All chemicals were purchased by chemical suppliers and used without further purification. All analytical reagent-grade solvents were purified by distillation. Dry solvents were prepared using customary literature procedures.[16] Thin layer chromatography (TLC): Riedel–de Haën silica gel F254 and Merck silica gel 60 F254. Detection: UV lamp and iodine chamber. Flash chromatography (FC): Merck silica gel 60 (230–400 mesh, 0.04–0.063 nm). Solvents were purified by distillation prior to use. UV/vis spectroscopy: Shimadzu UV-3102 PC UV/Vis/NIR scanning spectrophotometer; absorption maxima λ_{max} are given in nanometer. Mass spectrometry: Micromass Zabspec, FAB (LSIMS) mode, matrix 3-nitrobenzyl alcohol. NMR spectroscopy: JEOL JNM EX 400 and JEOL JNM GX 400 and Bruker Avance 300. The chemical shifts are given in parts per million relative to TMS. The resonance multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet) and m (multiplet), non-resolved and broad resonances as br. Elemental analysis (C, H, N): succeeded by combustion and gas chromatographical analysis with an EA 1110 CHNS analyser (CE Instruments). Fluorescence spectroscopy: Fluoromax3 Jobin Yvon Horiba, HORIBA Jobin Yvon GmbH, München. IR data: FT-IR Bruker Vector 22.

4.2. 5-Iodo-isophthalic acid (1)

$KMnO_4$ (21.67 g, 0.137 mol) was added to a suspension of 5-iodo-xylene (12 g, 0.0648 mol, 8.82 mL) in *tert*-butanol/H_2O (120 mL, 1:1). After heating the suspension for 1 h at 100 °C another $KMnO_4$ (21.67 g, 0.137 mol) was added. The suspension was heated at 100 °C for another 20 h and then cooled to rt. After filtration over Celite and washing with water the filtrate was reduced to one-third

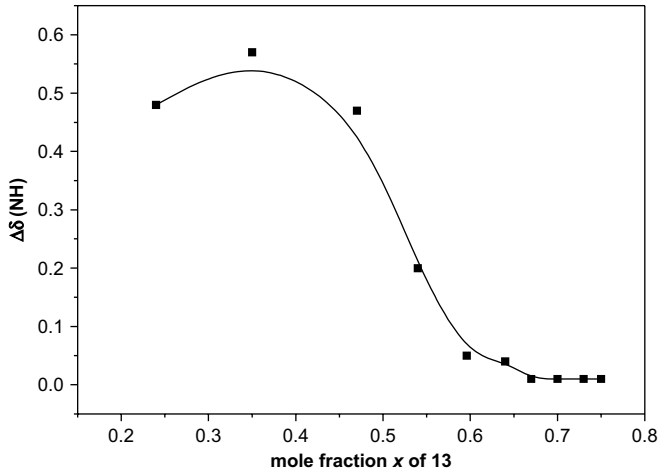


Figure 3. Job's plot analysis for the determination of 1:2 complex between *p*-OPE **9** and porphyrin **13**.

and acidified with concd HCl. The appearing white precipitate was dissolved in concd $NaHCO_3$ solution and washed three times with diisopropylether (100 mL). After further acidification with concd HCl the white precipitate was collected and dried at 80 °C overnight. Yield: 12.8 g (85%).

^{1}H NMR (DMSO-d_6, 400 MHz, rt): δ [ppm] 13.54 (br s, 2H, COOH), 8.40 (s, 3H). ^{13}C NMR (DMSO-d_6, 100.5 MHz, rt): δ [ppm] 165.2 (2C), 141.4 (2C), 133.1 (2C), 129.1 (1C), 94.8 (1C). EA: calculated for $C_8H_5O_4I$ (292.03): C 32.90, H 1.73; found: C 33.05, H 1.86. FTIR (diamond, rt): [cm^{-1}] 3535, 3440, 3085, 2645, 2542, 1710, 1624, 1571, 1461, 1292, 1212.32, 1159, 1107, 799, 751.

4.3. 5-Iodo-isophthaloyl dichloride (2)

A solution of 5-iodo-isophthalic acid **1** (1.5 g, 5.1 mmol) in thionyl chloride (30 mL) and *N*,*N*′-dimethylformamide (five drops) was refluxed for 6 h under dry conditions with subsequent removal of the excess of the thionyl chloride in vacuo. The residue was dried under high vacuum and yielded a red-brownish oil. Yield: 1.68 g (100%).

^{1}H NMR (DMSO-d_6, 400 MHz, rt): δ [ppm] 8.38 (s, 3H). ^{13}C NMR (DMSO-d_6, 100.5 MHz, rt): δ [ppm] 165.2 (2C), 141.4 (2C), 133.0 (2C), 129.1 (1C), 94.8 (1C).

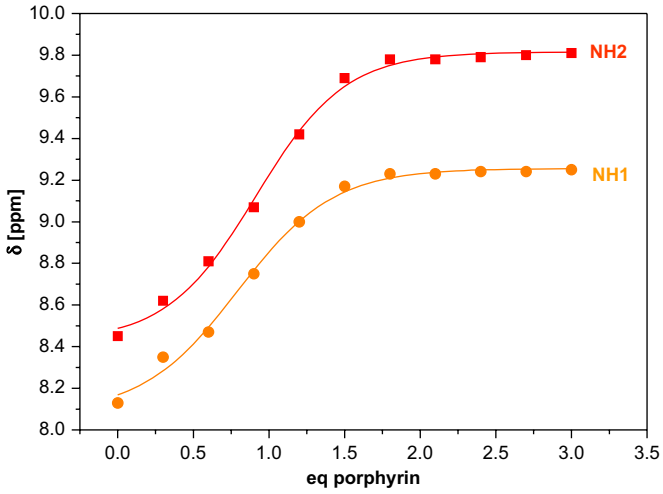


Figure 4. ^{1}H NMR titration plots of the chemical shifts of the NH1 and NH2 protons as a function of the amount of added porphyrin **13**.

Table 1
Association constants, r_{max} and Hill coefficients for the systems **7**:**13**, **8**:**13** and **9**:**13**

	log K_1 (mol^{-1} dm^3)	log K_2 (mol^{-1} dm^3)	r_{max}	η_H
7:**13**	5.00	10.05	0.80	0.67
8:**13**	5.79	10.03	0.51	0.34
9:**13**	6.40	12.05	0.48	0.32

4.4. *N*,*N*′-Bis[6-(3,3-dimethylbutyrylamino)pyridine-2-yl]-5-iodo-isophthalamide (4)

A solution of diacid **2** (1.68 g, 5.1 mmol), respectively, in dry THF (40 mL) was added dropwise to a solution of *N*-(6-aminopyridine-2-yl)-3,3-dimethylbutyramide (2.12 g, 10.24 mmol) and triethylamine (1.44 mL, 10.24 mmol) in dry THF (40 mL) at 0 °C. The solution was stirred at rt for 12 h, the residue filtered off and the solvent removed under reduced pressure. Purification by column chromatography on silica gel (CH_2Cl_2/ethyl acetate (2:1) as eluent) gave a yellowish solid. Yield: 3.23 g (94%).

^{1}H NMR (THF-d_8, 400 MHz, rt): δ [ppm] 9.73 (br s, 2H, NH), 9.09 (br s, 2H, NH), 8.46 (s, 1H), 8.45 (s, 2H), 8.00 (m, 4H), 7.73 (d, ^3J=8.1 Hz, 2H), 2.26 (s, 4H), 1.08 (s, 18H). ^{13}C NMR (THF-d_8, 100.5 MHz, rt): δ [ppm] 170.8 (2C), 164.2 (2C), 151.7 (2C), 151.1 (2C), 140.5 (2C), 140.3 (2C), 137.9 (2C), 127.1 (1C), 110.4 (2C), 110.1 (2C), 94.5 (1C), 50.7 (2C), 31.6 (2C), 30.0 (6C). MS (FAB, NBA): *m*/*z*=671 [M]$^+$. EA: calculated for $C_{30}H_{37}O_5N_6I\cdot H_2O$ (670.54): C 52.33, H 5.42, N 12.21; found: C 52.65, H 5.15, N 12.28. FTIR (diamond, rt): [cm^{-1}] 3429, 3303, 2957, 2929, 1690, 1584, 1516, 1447, 1365, 1298, 1156.

4.5. *N*,*N*′-Bis[6-(3,3-dimethylbutyrylamino)pyridine-2-yl]-5-trimethylsilylethynyl-isophthalamide (5)

Iodo-Hamilton receptor **4** (500 mg, 0.746 mmol) was dissolved under inert conditions in dry THF (12 mL) and NEt_3 (7 mL). Then $Pd(PPh_3)Cl_2$ (6 mg, 0.0075 mmol), PPh_3 (1 mg, 0.004 mmol) and CuI (4 mg, 0.022 mmol) were added at rt. After stirring the reaction mixture for 15 min to dissolve the catalysts trimethylsilylacetylene (88 mg, 0.895 mmol) was added dropwise over a period of 1 min. The reaction mixture was then stirred for another 24 h at rt, filtered and the solvent distilled under reduced pressure. The crude product was purified by column chromatography (CH_2Cl_2/EtOAc 7:1). Yield: 463 mg (97%).

^{1}H NMR (THF-d_8, 400 MHz, rt): δ [ppm] 9.68 (br s, 2H, NH), 9.09 (br s, 2H, NH), 8.47 (s, 1H), 8.19 (s, 2H), 8.03 (m, 4H), 7.72 (d, ^3J=8.0 Hz, 2H), 2.63 (s, 4H), 1.08 (s, 18H), 0.28 (s, 9H). ^{13}C NMR (THF-d_8, 100.5 MHz, rt): δ [ppm] 170.7 (2C), 164.7 (2C), 151.7 (2C), 151.1 (2C), 140.5 (2C), 136.5 (2C), 134.4 (2C), 127.9 (1C), 124.6 (1C), 110.4 (2C), 110.2 (2C), 104.3 (1C), 96.5 (1C), 50.7 (2C), 31.6 (2C), 30.0 (6C), −0.3 (3C). MS (FAB, NBA): *m*/*z*=642 [M]$^+$. FTIR (diamond, rt): [cm^{-1}] 3294, 2956, 2869, 2355, 1673, 1585, 1510, 1444, 1397, 1366, 1297, 1244, 1156, 802.

4.6. *N*,*N*′-Bis[6-(3,3-dimethylbutyrylamino)pyridine-2-yl]-5-ethynyl-isophthalamide (6)

TBAF in THF (0.226 mL, 0.76 mmol) was added dropwise to a solution of 443 mg (0.69 mmol) TMS protected acetylene Hamilton receptor **5** in dry THF (10 mL) at rt. After stirring for 3 h the solvent was evaporated and the residue purified by column chromatography (CH_2Cl_2/EtOAc 4:1). All purification steps were done at rt. Yield: 378 mg (96%).

^{1}H NMR (THF-d_8, 400 MHz, rt): δ [ppm] 9.70 (br s, 2H, NH), 9.08 (br s, 2H, NH), 8.48 (s, 1H), 8.22 (s, 2H), 8.03 (m, 4H), 7.73 (d, ^3J=8.0 Hz, 2H), 3.83 (s, 1H), 2.70 (s, 4H), 1.08 (s, 18H). ^{13}C NMR (THF-d_8, 100.5 MHz, rt): δ [ppm] 170.8 (2C), 164.7 (2C), 151.7 (2C), 151.2 (2C), 140.5 (2C), 136.6 (2C), 134.6 (2C), 127.9 (1C), 124.0 (1C), 110.4

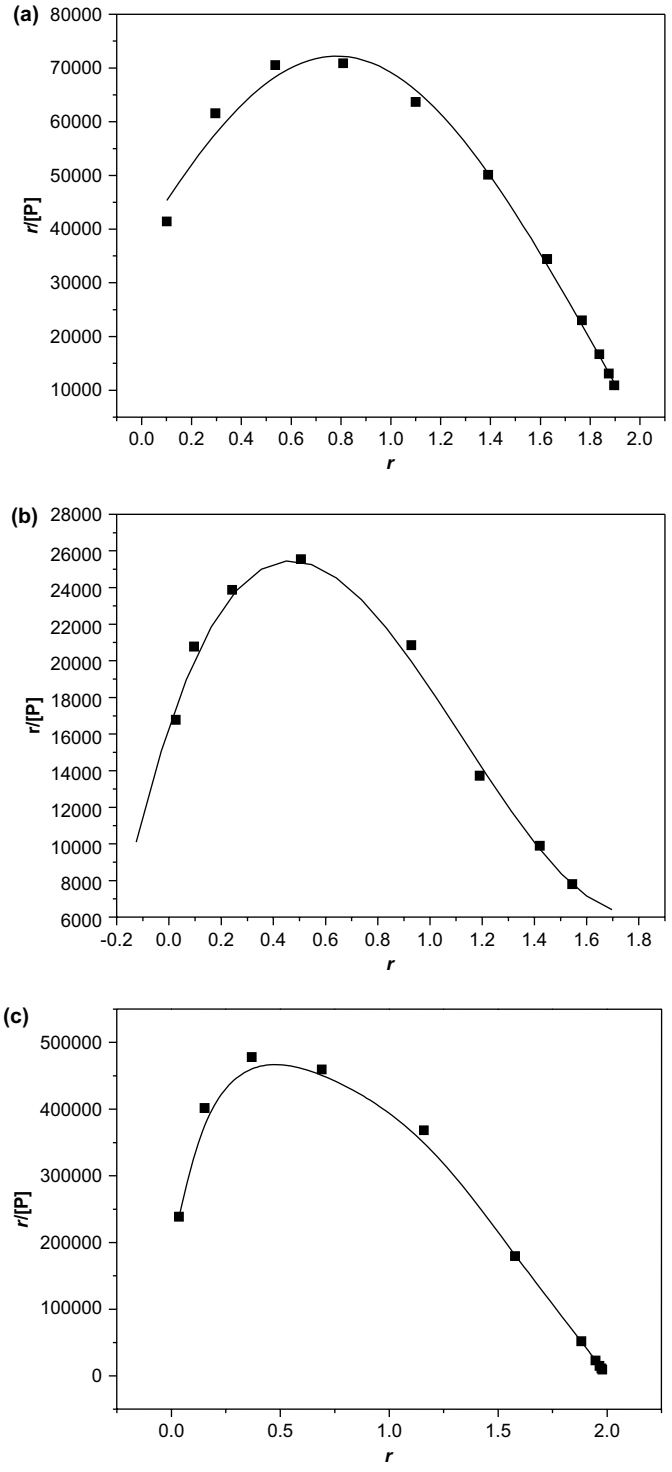


Figure 5. Scatchard plots for the *p*-OPE systems and porphyrin **13**. (a) **7**:**13**, (b) **8**:**13**, (c) **9**:**13**.

(2C), 110.2 (2C), 82.7 (1C), 80.8 (1C), 50.7 (2C), 31.6 (2C), 30.0 (6C). MS (FAB, NBA): m/z=570 $[M]^+$. FTIR (diamond, rt): [cm^{-1}] 3295, 2954, 2865, 2360, 1673, 1555, 1512, 1446, 1396, 1297, 1240, 1156, 1132, 800.

4.7. Bis-*N*,*N*′-bis[6-(3,3-dimethylbutyrylamino)pyridine-2-yl]-5-ethynyl-isophthalamide (7)

$Pd(PPh_3)_2Cl_2$ (2 mg, 0.003 mmol) and CuI (2 mg, 0.009 mmol) were dissolved in dry THF (12 mL) and NEt_3 (5 mL) before *N*,*N*′-

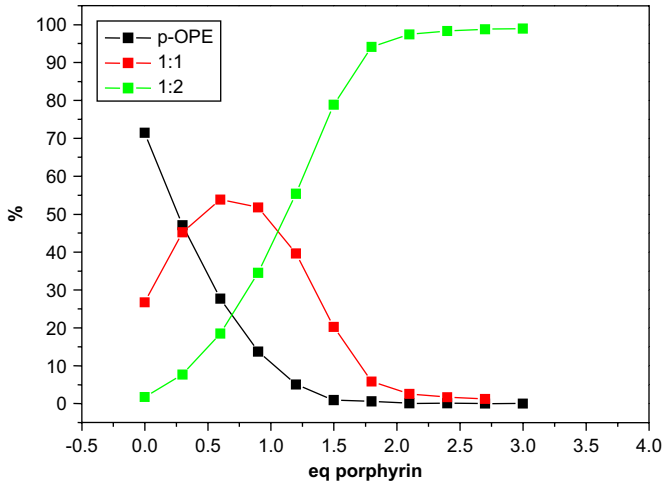


Figure 6. Distribution in percent of **9** as free core and within the complexes **9**:**13***n* (*n*=1–2) as a function of the amount of added porphyrin obtained from analysis of the titration plots using the computer program Chem-Equili.[12] The total concentration of **9** within the mixtures is 3.3 mM.

bis[6-(3,3-dimethylbutyrylamino)pyridine-2-yl]-5-ethynyl-isopht halamide **6** (172 mg, 0.302 mmol) was added at once. The mixture was stirred at rt for 72 h, filtered and the solvent was distilled. The crude product was purified using column chromatography (CH_2Cl_2, 5% MeOH). Yield: 163 mg (95%).

^{1}H NMR (THF-d_8, 400 MHz, rt): δ [ppm] 9.82 (br s, 4H, NH), 9.16 (br s, 4H, NH), 8.58 (s, 2H), 8.35 (s, 4H), 8.04 (m, 8H), 7.74 (d, ^3J=8,0 Hz, 4H), 2.27 (s, 8H), 1.09 (s, 36H). ^{13}C NMR (THF-d_8, 100.5 MHz, rt): δ [ppm] 170.8 (4C), 164.8 (4C), 151.8 (4C), 151.1 (4C), 140.6 (4C), 136.8 (4C), 135.3 (4C), 129.1 (2C), 122.8 (2C), 110.5 (4C), 110.2 (4C), 81.4 (2C), 75.2 (2C), 50.7 (4C), 31.6 (4C), 30.0 (12C). MS (FAB, NBA): m/z=1135 $[M]^+$. FTIR (diamond, rt): [cm^{-1}] 3726, 3307, 2970, 2360, 2342, 1738, 1680, 1585, 1513, 1446, 1365, 1298, 1233, 1156, 1131, 1085, 799.

4.8. 1,4-[Bis-*N*,*N*′-bis[6-(3,3-dimethylbutyrylamino)pyridine-2-yl]-5-ethynyl-isophthalamide]benzene (8)

To a solution of 1,4-diiodobenzene (27 mg, 0.08 mmol) and PPh_3 (1 mg, 0.004 mmol) in dry THF (10 mL) and HN*i*-Pr_2 (4 mL) $Pd(PPh_3)Cl_2$ (1 mg, 0.002 mmol) and CuI (1 mg, 0.005 mmol) were added at rt. After 15 min of stirring this mixture *N*,*N*′-bis[6-(3,3-dimethylbutyrylamino)

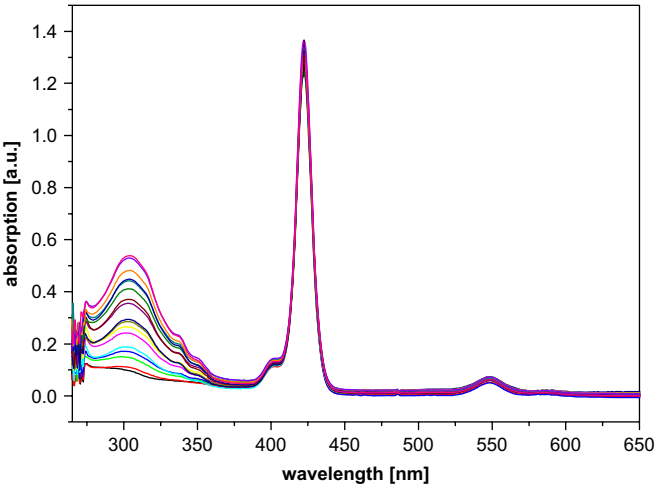


Figure 7. UV/vis titration of **13** (c=4.5×10^{-6} mol/L) with variable concentrations of *p*-OPE **8** starting from c_1=4.15×10^{-7} mol/L to c_{15}=1.35×10^{-5} mol/L at rt in CH_2Cl_2.

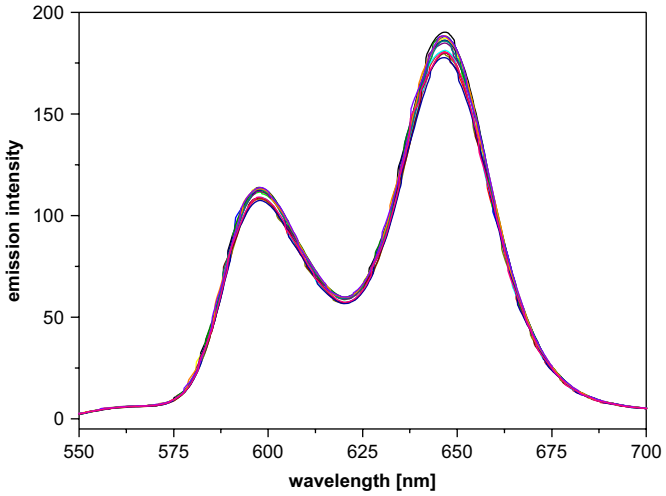


Figure 8. Fluorescence emission titration of porphyrin **13** with *p*-OPE **8** corresponding to the conditions of the absorption titration in Figure 6.

pyridin-2-yl]-5-ethynyl-isophthalamide **6** (100 mg, 0.176 mmol) was added at once and the mixture was stirred for 60 h at rt. After filtration, the solvent was distilled and the remainder purified by column chromatography (CH_2Cl_2/EtOAc/MeOH 4:1:0.02). Yield: 152 mg (72%).

^{1}H NMR (THF-d_8, 400 MHz, rt): δ [ppm] 9.79 (br s, 4H, NH), 9.12 (br s, 4H, NH), 8.55 (s, 2H), 8.33 (s, 4H), 8.04 (m, 8H), 7.73 (t, ^3J=6.5 Hz, 4H), 7.63 (s, 4H), 2.28 (s, 8H), 1.09 (s, 36H). ^{13}C NMR (THF-d_8, 100.5 MHz, rt): δ [ppm] 170.8 (4C), 164.8 (4C), 151.7 (4C), 151.1 (4C), 140.6 (4C), 136.8 (4C), 135.3 (4C), 133.8 (4C), 132.6 (2C), 129.5 (2C), 122.8 (2C), 110.5 (4C), 110.2 (4C), 81.4 (2C), 75.3 (2C), 50.7 (4C), 31.6 (4C), 30.0 (12C). MS (FAB, NBA): m/z=1210 [M]$^+$. UV/vis (CH_2Cl_2): λ_{max}=304 nm. FTIR (diamond, rt): [cm^{-1}] 3732, 3286, 2970, 2360, 2342, 1738, 1679, 1585, 1510, 1446, 1365, 1297, 1231, 1218, 1156, 1131, 799.

4.9. 1,4-[Bis-*N,N*′-bis[6-(3,3-dimethylbutyrylamino)pyridine-2-yl]-5-ethynyl-isophthalamide]-2,5-bisoctyloxy benzene (9)

1,4-Diiodo-2,5-bisoctyloxybenzene (32 mg, 0.052 mmol), $Pd(PPh_3)_2Cl_2$ (3 mg, 0.004 mmol) and CuI (2 mg, 0.01 mmol) were dissolved in dry THF (15 mL) and $HNEt_2$ (5 mL). Then *N,N*′-bis[6-(3,3-dimethylbutyrylamino)pyridine-2-yl]-5-ethynyl-isophthalamide **6** (65 mg, 0.115 mmol) was added at once. The reaction mixture was then stirred for 3.5 h at 70 °C and then for 48 h at rt. After filtration and evaporation of the solvents the crude product was purified by column chromatography (CH_2Cl_2/EtOAc/MeOH 5:1:0.01). Yield: 102 mg (75%).

^{1}H NMR (THF-d_8, 400 MHz, rt): δ [ppm] 9.77 (br s, 4H, NH), 9.12 (br s, 4H, NH), 8.48 (s, 2H), 8.28 (s, 4H), 8.06 (d, ^3J=6.7 Hz, 4H), 8.03 (t, ^3J=6.8 Hz, 4H), 7.74 (d, ^3J=8.1 Hz, 4H), 7.19 (s, 2H), 4.12 (t, ^3J=6.4 Hz, 4H), 2.27 (s, 4H), 1.73 (m, 12H), 1.30 (m, 12H), 1.09 (s, 36H), 0.82 (t, ^3J=6.7 Hz, 6H). ^{13}C NMR (THF-d_8, 100.5 MHz, rt): δ [ppm] 170.8 (4C), 164.9 (4C), 154.8 (2C), 151.7 (4C), 151.1 (4C), 140.5 (4C), 136.6 (4C), 134.2 (4C), 129.5 (2C), 125.2 (2C), 117.6 (2C), 114.7 (2C), 110.4 (4C), 110.2 (4C), 93.9 (2C), 88.6 (2C), 70.2 (2C), 50.7 (4C), 31.6 (4C), 32.7 (2C), 31.6 (12C), 30.0 (2C), 29.8 (2C), 25.5 (2C), 23.4 (2C), 14.4 (2C). MS (FAB, NBA): m/z=1468 [M]$^+$. UV/vis (CH_2Cl_2): λ_{max}=304, 401 nm. FTIR (diamond, rt): [cm^{-1}] 3303, 2954, 2868, 2359, 1738, 1681, 1586, 1681, 1589, 1503, 1446, 1366, 1323, 1297, 1239, 1156, 1083, 800.

4.10. 5-(4-Ethynyl-trimethylsilyl-phenyl)-10,15,20-(3,5-dimethoxy-phenyl)-porphyrin (10)

A solution of pyrrole (1.39 mL, 0.02 mol), 3,5-dimethoxy benzaldehyde (2.46 g, 0.015 mol) and 4-trimethylsilylethynylbenzaldehyde (1 g, 0.005 mol) in 500 mL of dichloromethane was stirred for 15 min. Then TFA (578 μL, 0.015 mol) was added and the reaction mixture stirred for another 60 min before NEt_3 (1.25 mL, 0.048 mol) was added for neutralization. DDQ (3.405 g, 0.015 mol) was added after stirring for 8 min. The reaction mixture was stirred for 15 h under atmospheric conditions. The solvent was removed under evaporation and filtered over silica in dichloromethane. The residue was purified with column chromatography on silica (hexanes/EtOAc 4:1). The product was obtained by crystallization in pentane. Yield: 200 mg (5%).

^{1}H NMR ($CDCl_3$, 400 MHz, rt): δ [ppm] 8.98 (d, ^3J=4.6 Hz, 2H), 8.97 (s, 4H), 8.83 (d, ^3J=4.6 Hz, 2H), 8.20 (d, ^3J=8.3 Hz, 6H), 7.91 (d, ^3J=8.3, 2H), 7.41 (s, 6H), 6.92 (s, 6H), 3.98 (s, 18H), 0.40 (s, 9 H), −2.80 (s, 2H, NH). ^{13}C NMR ($CDCl_3$, 100.5 MHz, rt): δ [ppm] 158.9 (3C), 144.0 (6C), 142.5 (2C), 134.4 (1C), 131.1 (2C), 130.4 (16C), 122.6 (3C), 119.9 (1C), 119.2 (1C), 113.9 (6C), 105.0 (1C), 100.2 (3C), 95.6 (1C), 55.6 (6C), 0.1 (3C). MS (FAB, NBA): m/z=891 [M]$^+$. UV/vis (CH_2Cl_2): λ_{max} (log ε) [nm]=422 (5.77), 516 (4.52), 555 (4.29), 592 (4.18), 645 nm. FTIR (diamond, rt): [cm^{-1}] 3008, 2970, 2927, 2854, 2360, 2341, 2155, 1738, 1590, 1454, 1420, 1365, 1296, 1229, 1216, 1205, 1154, 1063, 1020, 973, 919, 860, 801, 758, 736, 711.

4.11. 5-(4-Ethynyl-trimethylsilyl-phenyl)-10,15,20-(3,5-dimethoxy-phenyl)-porphyrinato zinc II (11)

Porphyrin **10** (176 mg, 0.198 mmol) and zinc(II) acetate (130 mg, 0.59 mmol) were dissolved in THF (50 mL) and refluxed for 4 h. After cooling to rt the solvent was removed and the occurring residue was purified by column chromatography on silica gel (CH_2Cl_2/EtOAC 5:1). Yield: 164 mg (87%).

^{1}H NMR ($CDCl_3$, 400 MHz, rt): δ [ppm] 9.02 (d, ^3J=4.6 Hz, 2H), 9.01 (s, 4H), 8.90 (d, ^3J=4.6 Hz, 2H), 8.16 (d, ^3J=8.3 Hz, 6H), 7.87 (d, ^3J=8.3 Hz, 2H), 7.30 (s, 6H), 6.74 (s, 6H), 3.83 (s, 18H), 0.38 (s, 9H). ^{13}C NMR ($CDCl_3$, 100.5 MHz, rt): δ [ppm] 158.6 (3C), 150.1 (2C), 150.0 (4C), 144.5 (6C), 143.2 (2C), 134.3 (1C), 132.2 (2C), 132.1 (2C), 131.6 (2C), 130.2 (4C), 122.3 (3C), 120.9 (1C), 120.2 (1C), 113.8 (6C), 105.1 (1C), 100.0 (3C), 95.4 (1C), 55.6 (6C), 0.1 (3C). MS (FAB, NBA): m/z=953 [M]$^+$. UV/vis (CH_2Cl_2): λ_{max} (log ε) [nm]=422 (5.69), 548 (4.38), 591 (3.64). FTIR (diamond, rt): [cm^{-1}] 3006, 2970, 2945, 2360, 2342, 2155, 1738, 1589, 1508, 1494, 1454, 1421, 1365, 1351, 1228, 1217, 1205, 1153, 1063, 1028, 1001, 938, 860, 810, 797, 762, 740, 720.

4.12. 5-(4-Ethynyl-phenyl)-10,15,20-(3,5-dimethoxy-phenyl)-porphyrinato zinc II (12)

Porphyrin **11** (160 mg, 0.168 mmol) was dissolved in dry THF before TBAF (200 μL, 0.185 mmol of a 1 M solution in THF) was added at once. After stirring for 2 h a few drops of water were added. After evaporation of the solvent column chromatography on silica gel (CH_2Cl_2/EtOAc 4:1) was used to purify the desired product. Yield: 135 mg (91%).

^{1}H NMR ($CDCl_3$, 400 MHz, rt): δ [ppm] 9.02 (d, ^3J=4.6 Hz, 2H), 9.01 (s, 4H), 8.90 (d, ^3J=4.6 Hz, 2H), 8.17 (d, ^3J=8.3 Hz, 6H), 7.87 (d, ^3J=8.3 Hz, 2H), 7.33 (s, 6H), 6.79 (s, 6H), 3.86 (s, 19H). ^{13}C NMR ($CDCl_3$, 100.5 MHz, rt): δ [ppm] 158.6 (3C), 150.1 (2C), 150.0 (4C), 144.5 (6C), 143.5 (2C), 134.3 (1C), 132.2 (2C), 132.1 (2C), 131.6 (2C), 130.4 (4C), 121.3 (3C), 120.9 (1C), 120.2 (1C), 113.8 (6C), 100.0 (3C), 83.3 (1C), 78.1 (1C), 55.6 (6C). MS (FAB, NBA): m/z=881 [M]. UV/vis (CH_2Cl_2): λ_{max} (log ε) [nm]=422 (5.78), 547 (4.49), 593 (3.81). FTIR (diamond, rt): [cm^{-1}] 2999, 2970, 2940, 2836, 2580, 2360, 2342, 1738, 1589, 1525, 1494, 1453, 1420, 1365, 1350, 1317, 1230, 1216, 1203, 1152, 1063, 1001, 954, 938, 860, 811, 797, 762, 738, 720.

4.13. 5-(*E*-Ethynyl-phenyl-cyanuric-phenyl)-10,15,20-(3,5-dimethoxy-phenyl)-porphyrinato zinc II (13)

4-Iodophenyl isocyanuric acid (11 mg, 0.032 mmol), Pd_2dba_3 (1 mg, 0.0006 mmol), $AsPh_3$ (0.2 mmol, 0.0006 mmol) and CuI (0.5 mg, 0.002 mmol) were dissolved in dry THF (8 mL) and NEt_3 (3 mL). Then porphyrin **12** (31 mg, 0.035 mmol) was added and the reaction mixture was stirred under inert conditions and with exclusion of light for 3 days. After removing the precipitates and distillation of the solvent the residue was purified by column chromatography ($CH_2Cl_2 \rightarrow CH_2Cl_2$/EtOAc/THF 2:1:1). Yield: 28 mg (81%).

^{1}H NMR (THF-d_8, 400 MHz, rt): δ [ppm] 10.69 (br s, 2H, NH), 8.98 (d, ^3J=4.6 Hz, 2H), 8.95 (s, 4H), 8.87 (d, ^3J=4.6 Hz, 2H), 8.25 (d, ^3J=8.1 Hz, 6H), 7.96 (d, ^3J=8.1 Hz, 6H), 7.78 (d, ^3J=8.7 Hz, 2H), 7.38 (s, 6H), 7.07 (d, ^3J=8.6 Hz, 2H), 6.91 (s, 6H), 3.94 (s, 18H). ^{13}C NMR (THF-d_8, 100.5 MHz, rt): δ [ppm] 159.8 (3C), 150.8 (2C), 150.7 (1C), 150.5 (2C), 150.1 (4C), 149.9 (1C), 146.0 (6C), 144.9 (2C), 138.6 (1C), 135.6 (2C), 132.2 (2C), 131.8 (2C), 131.7 (2C), 130.4 (4C), 130.1 (2C), 124.3 (3C), 123.0 (1C), 121.4 (1C), 120.3 (1C), 114.6 (6C), 100.2 (3C), 94.8 (1C), 90.2 (1C), 55.6 (6C). MS (FAB, NBA): m/z=1084 $[M]^+$. UV/vis (CH_2Cl_2): λ_{max} (log ε) [nm]=43 (5.16), 548 (3.82), 588 (3.10). FTIR (diamond, rt): [cm^{-1}] 3000, 2970, 2949, 2360, 2342, 1795, 1738, 1721, 1590, 1548, 1515, 1488, 1489, 1421, 1366, 1351, 1229, 1216, 1204, 1153, 1107, 1062, 1026, 999, 953, 937, 825, 797, 757, 740, 723.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft (SFB 583: Redoxaktive Metallkomplexe – Reaktivitätssteuerung durch molekulare Architekturen and Exzellenzcluster EAM-Engineering of Advanced Materials) for financial support.

References and notes

(1). (a) Detert, H.; Schollmeyer, D.; Sugiono, E. *Eur. J. Org. Chem.* **2001**, 2927–2938; (b) Weder, C.; Wrighton, M. S. *Macromolecules* **1996**, *29*, 5157–5165; (c) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539–541; (d) Ohmori, Y.; Uchida, M.; Muro, K.; Katsumi, Y. *Jpn. J. Appl. Phys.* **1991**, *30*, 1938–1940; (e) Berggren, M.; Inganas, O.; Gustafsson, G.; Rasmusson, J.; Andersson, M. R.; Hjertberg, T.; Wennerström, O. *Nature* **1994**, *372*, 444–446; (f) Rajca, A.; Rajca, S.; Pink, M.; Miyasaka, M. *Synlett* **2007**, 1799–1822; (g) Murphy, A. R.; Fréchet, J. M. J. *Chem. Rev.* **2007**, *107*, 1066–1096; (h) Ajayaghosh, A.; Praveen, V. K. *Acc. Chem. Res.* **2007**, *40*, 644–656.

(2). (a) Tomović, Z.; van Dongen, J.; George, S. J.; Xu, H.; Pisula, W.; Leclere, W.; Smulders, M. M. J.; de Feyter, S.; Meijer, E. W.; Schenning, A. H. P. J. *J. Am. Chem. Soc.* **2007**, *129*, 16190–16196; (b) Watson, M. D.; Fechtenkötter, A.; Müllen, K. *Chem. Rev.* **2001**, *101*, 1267–1300; (c) Grimsdale, A. C.; Müllen, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 5592–5629; (d) Schenning, A. P. H. J.; Meijer, E. W. *Chem. Commun.* **2005**, 3245–3258; (e) Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. J. *Chem. Rev.* **2005**, *105*, 1491–1546; (f) Wu, J.; Pisula, W.; Müllen, K. *Chem. Rev.* **2007**, *107*, 718–747; (g) Yamamoto, Y.; Fukushima, T.; Suna, Y.; Ishii, N.; Saeki, A.; Seki, S.; Tagawa, S.; Taniguchi, M.; Kawai, T.; Aida, T. *Science* **2006**, *314*, 1761–1764; (h) Yamamoto, Y.; Fukushima, T.; Jin, W.; Kosaka, A.; Hara, T.; Nakamura, T.; Saeki, A.; Seki, S.; Tagawa, S.; Aida, T. *Adv. Mater.* **2006**, *18*, 1297–1300; (i) Xiao, S.; Tang, J.; Beetz, T.; Guo, X.; Tremblay, N.; Siegrist, T.; Zhu, Y.; Steigerwald, M.; Nuckolls, C. *J. Am. Chem. Soc.* **2006**, *128*, 10700–10701; (j) Shklyarevskiy, I. O.; Jonkheijm, P.; Stutzmann, N.; Wasserberg, D.; Wondergem, H. J.; Christianen, P. C. M.; Schenning, A. P. H. J.; de Leeuw, D. M.; Tomović, Z.; Wu, J.; Müllen, K.; Maan, J. C. *J. Am. Chem. Soc.* **2005**, *127*, 16233–16237; (k) Jonkheijm, P.; Stutzmann, N.; Chen, Z.; de Leeuw, D. M.; Meijer, E. W.; Schenning, A. P. H. J.; Würthner, F. *J. Am. Chem. Soc.* **2006**, *128*, 9535–9540.

(3). (a) Secker, D.; Weber, H. *Phys. Status Solidi B* **2007**, *244*, 4176–4180; (b) Lörtscher, E.; Weber, H.; Riel, H. *Phys. Rev. Lett.* **2007**, *98*, 176807; (c) Ochs, R.; Secker, D.; Elbing, M.; Mayor, M.; Weber, H. *Faraday Discuss.* **2006**, *131*, 281–289; (d) Elbing, M.; Ochs, R.; Koentopp, M.; Fischer, M.; von Hänisch, C.; Weigend, F.; Evers, F.; Weber, H.; Mayor, M. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 8815–8820; (e) van Ruitenbeek, J.; Scheer, E.; Weber, H. Contacting Individual Molecules Using Mechanically Controllable Break Junctions. In *Introducing Molecular Electronics*; Cuniberti, G., Fagas, G., Richter, K., Eds.; Springer: Berlin, Heidelberg, 2005; pp 253–274; (f) Mas-Torrent, M.; den Boer, D.; Durkut, M.; Hadley, P.; Schenning, A. P. H. J. *Nanotechnology* **2004**, *15*, 265–269; (g) Akagi, K.; Piao, G.; Kaneko, S.; Sakamaki, K.; Sirakawa, H.; Kyotani, M. *Science* **1998**, *282*, 1683–1686.

(4). Xia, Y.; Yang, P.; Sun, Y.; Wu, Y.; Mayers, B.; Gates, B.; Yin, Y.; Kim, F.; Yan, H. *Adv. Mater.* **2003**, *15*, 353–389.

(5). *Acc. Chem. Res.* **2002**, *36*.

(6). (a) Chang, S.-K.; Hamilton, A. D. *J. Am. Chem. Soc.* **1988**, *110*, 1318–1319; (b) Hager, K.; Franz, A.; Hirsch, A. *Chem.—Eur. J.* **2006**, *12*, 2663–2679; (c) Hager, K.; Hartnagel, U.; Hirsch, A. *Eur. J. Org. Chem.* **2007**, 1942–1956; (d) Maurer, K.; Hager, K.; Hirsch, A. *Eur. J. Org. Chem.* **2006**, 3338–3347; (e) Franz, A.; Bauer, W.; Hirsch, A. *Angew. Chem.* **2005**, *117*, 1588–1591; *Angew. Chem., Int. Ed.* **2005**, *44*, 1564–1567; (f) Wessendorf, F.; Gnichwitz, J.-F.; Sarova, G. H.; Hager, K.; Hartnagel, U.; Guldi, D. M.; Hirsch, A. *J. Am. Chem. Soc.* **2007**, *129*, 16057–16071; (g) Berl, V.; Schmutz, M.; Krische, M. J.; Khoury, R. G.; Lehn, J. M. *Chem.—Eur. J.* **2002**, *8*, 1227–1244.

(7). Boyd, A. S. F.; Carroll, J. B.; Cooke, G.; Garety, J. F.; Jordan, B. J.; Mabruk, S.; Rosaira, G.; Rotellob, V. M. *Chem. Commun.* **2005**, 2468–2470.

(8). (a) Nagy, A.; Novak, Z.; Kotschy, A. *J. Organomet. Chem.* **2005**, *690*, 4453–4461; (b) Tykwinski, R. R. *Angew. Chem., Int. Ed.* **2003**, *42*, 1566–1568.

(9). (a) Littler, B. J.; Ciringh, Y.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 2864–2872; (b) Geier, R. G., III; Lindsey, J. S. *J. Chem. Soc., Perkin Trans. 2* **2001**, 677–686; (c) Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Maguerettaz, A. M. *J. Org. Chem.* **1987**, *52*, 827–836; (d) Lindsey, J. S.; Wagner, R. W. *J. Org. Chem.* **1989**, *54*, 828–836; (e) Lindsey, J. S.; MacCrum, K. A.; Thyonas, J. S.; Chuang, Y.-Y. *J. Org. Chem.* **1994**, *59*, 579–587.

(10). (a) Sarova, G. H.; Hartnagel, U.; Balbinot, D.; Sali, S.; Jux, N.; Hirsch, A.; Guldi, D. M. *Chem.—Eur. J.* **2008**, *14*, 3137–3145; (b) Sgobba, V.; Rahman, G. M. A.; Guldi, D. M.; Jux, N.; Campidelli, S.; Prato, M. *Adv. Mater.* **2006**, *18*, 2264–2269; (c) Ehli, C.; Rahman, G. M. A.; Jux, N.; Balbinot; Guldi, D. M.; Paolucci, F.; Marcaccio, M.; Paolucci, D.; Melle-Franco, M.; Zerbetto, F.; Campidelli, S.; Prato, M. *J. Am. Chem. Soc.* **2006**, *128*, 11222–11231.

(11). (a) Perlmutter-Hayman, B. *Acc. Chem. Res.* **1986**, *19*, 90–96; (b) Schneider, H.-J.; Yatsimirsky, A. *Principles and Methods in Supramolecular Chemistry*; Wiley: Chichester, UK, 2000.

(12). (a) Solov'ev, V. P.; Vnuk, E. A.; Strakhova, N. N.; Reavsky, O. A. *VINITI*, Moscow, 1991; (b) Solov'ev, V. P.; Baulin, V. E.; Strahova, N. N.; Kazachenko, V. P.; Belsky, V. K.; Varnek, A. A.; Volkova, T. A.; Wipff, G. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1489–1498.

(13). (a) Guldi, D. M.; Zilbermann, I.; Anderson, G.; Li, A.; Balbinot, D.; Jux, N.; Hatzimarinaki, M.; Hirsch, A.; Prato, M. *Chem. Commun.* **2004**, 726–727; (b) Balbinot, D.; Atalick, S.; Guldi, D. M.; Hatzimarinaki, M.; Hirsch, A.; Jux, N. *J. Phys. Chem. B* **2003**, *107*, 13273–13279; (c) Guldi, D. M.; Rahman, G. M. A.; Prato, M.; Jux, N.; Qin, S.; Ford, W. *Angew. Chem.* **2005**, *117*, 2051–2054; *Angew. Chem., Int. Ed.* **2005**, *44*, 2015–2018.

(14). Hirst, A. R.; Coates, I. A.; Boucheteau, T. R.; Miravet, J. F.; Escuder, B.; Castelletto, V.; Hamley, I. W.; Smith, D. K. *J. Am. Chem. Soc.* **2008**, *130*, 9113–9121.

(15). (a) Martin, N.; Sanchez, L.; Herranz, M. A.; Illescas, B.; Guldi, D. M. *Acc. Chem. Res.* **2007**, *40*, 1015–1024; (b) Van der Pol, C.; Bryce, M. R.; Wielopolski, M.; Atienza-Castellanos, C.; Guldi, D. M.; Filippone, S.; Martin, N. *J. Org. Chem.* **2007**, *72*, 6662–6671; (c) Atienza-Castellanos, C.; Wielopolski, M.; Guldi, D. M.; van der Pol, C.; Bryce, M. R.; Filippone, S.; Martin, N. *Chem. Commun.* **2007**, 5164–5166; (d) Atienza, C.; Martin, N.; Wielopolski, M.; Haworth, N.; Clark, T.; Guldi, D. M. *Chem. Commun.* **2006**, 3202–3204.

(16). Perrin, D. D.; Amarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: Oxford, 1988.