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# Hydrogen-Bonding Induced Cooperative Effect on the Energy Transfer in Helical Polynorbornenes Appended with Porphyrin-Containing Amidic Alanine Linkers

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**Abstract:** Polynorbornenes appended with porphyrins containing a range of different linkers are synthesized. The use of bisamidic chiral alanine linkers between the pending porphyrins and the polymeric backbone has been shown to bring the adjacent porphyrin chromophores to more suitable orientation for exciton coupling owing to hydrogen bonding between the adjacent linkers. The hydrogen bonding between the adjacent pendants in these polymers may induce a cooperative effect and therefore render single-handed helical structures for these polymers. Such a cooperative effect is reflected in the enhancement of FRET efficiencies between zinc–porphyrin and free base porphyrin in random copolymers.

**Keywords:** energy transfer · helical structures · hydrogen bonds · porphyrinoids · ring-opening polymerization

## Introduction

Numerous model systems containing porphyrin donor–acceptor arrays have offered a platform to mimic biological light harvesting process.[1] Fluorescence resonance energy transfer (FRET) between zinc–porphyrin and free base porphyrin dyads with covalent[2] or noncovalent[3] linkers is well documented. Oligomers having linear, two-dimensional, as well as dendritic arrangements of chromophores have been adopted to simulate this important process.[4,5] Porphyrin arrays appended on polyisocyanides,[6] polypeptides,[7] cellulose,[8] poly(*N*-propargylamide)s,[9] polyacrylates,[10] and polynorbornenes[11] have been explored.

Polynorbornenes (PNBs) with a variety of pendant groups have been extensively investigated for photoinduced electron transfer,[12] liquid crystal,[13] nonlinear optical,[14,15] and possible molecular switching[16] applications. The relatively rigid polymeric backbone of PNBs provides a supporting framework for the pending groups coherently aligned towards the same direction.[11–16] We recently established that PNBs having *endo*-fused *N*-arylpyrrolidene pendants, obtained by Grubbs I catalyst mediated ring-opening metathesis polymerization[17] of the corresponding norbornene derivatives, adopt comblike structures with homogeneous tacticity and all double bonds in *trans* configuration.[11a,15] The corresponding double-stranded poly(bisnorbornene)s or ladderphanes were prepared accordingly,[18] single-handed helical polymers[19] being obtained when the chiral substituents are incorporated into these polymers. Each of the monomeric units spans about 5.5 Å in these polymers.[15a] Exciton coupling,[11a,18c] excimer formation,[18c] fluorescence quenching,[11a] or enhancement in second-order optical nonlinearity[15] readily occurs in these polymers when photoactive chromophores are used as pendants or linkers. For example, PNBs with certain porphyrin pendants exhibit Soret band splitting and significant fluorescence quenching owing to interactions between these chromophores.[11a,18c] It is envisaged that

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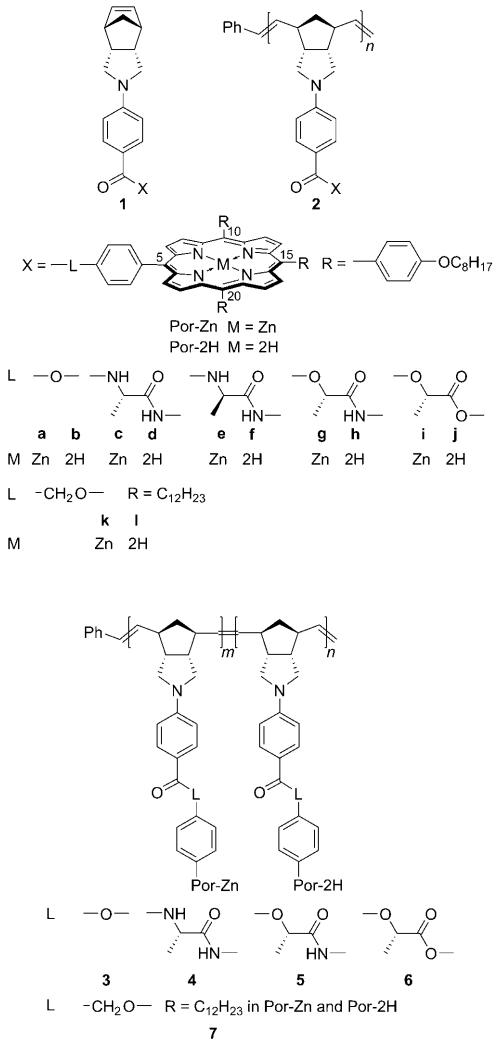
PNBs containing both donor and acceptor pending chromophores may undergo efficient energy and electron transfer between these photoactive species.

Hydrogen bonding offers a powerful arsenal to assemble different kinds of connectivity so that an intrinsically flexible structure can be transformed into a more ordered robust motif.[20] The amidic linkage is particularly attractive to furnish a range of new classes of folded oligomers. Abiotic supramolecular scaffolds with well-defined secondary structures can thus be designed and executed. Oligoamides derived from enantiomerically pure amino acid residues have been the archetype of helical foldamers[21] as well as sheet-like architectures.[22] Amalgamations of amino acid or peptide pendants onto polyisocyanides[23] and poly(phenylacetylene)s[24] are known to induce single-handed helicity of the polymers. The use of hydrogen bonding to form supramolecular systems can bring the attached chromophores into close proximity so that FRET or photoinduced electron transfer can readily take place.[25]

The relative distance and orientation of the porphyrin moieties may dictate the photophysical behavior of a light-harvesting system.[26] We envisioned that the introduction of chiral amino acid linkers between the pendant chromophores and the PNB backbone would increase the robustness of the polymer as a result of hydrogen bonding between amino acid residues. Strong interactions between chromophores might be expected because hydrogen bonding may bring the adjacent chromophores into a more suitable orientation for exciton coupling. Herein, we report a systematic study on the intramolecular energy transfer in a series of zinc–porphyrin and free base porphyrin-appended random copolymers with a range of different linkers.




## Results and Discussion

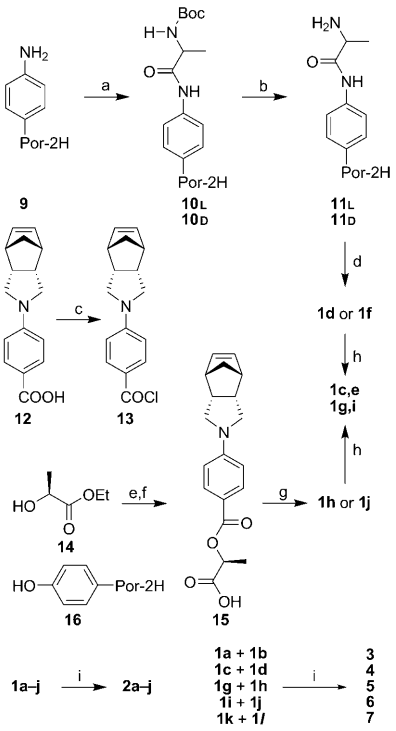
### Synthesis

A series of porphyrin-appended PNBs **2** incorporated with and without L-, D-alanine, or L-lactate linkers were synthesized. Random copolymers **3–7** containing zinc–porphyrin and free base porphyrin pendants with and without chiral linkers described above were used for energy transfer investigations. The details are summarized in Scheme 1 and the results are outlined in Table 1.

The $^1$H NMR spectra of monomers **1** and polymers **2–7** are worthy of comment. The olefinic protons in the polymeric backbones appeared in the $^1$H NMR spectra around $\delta = 5.2$ ppm as a broad symmetrical peak, which is similar to those of related polymers.[11a,15] These results indicate that the alkenes in the polymer backbone have *trans* configuration. Similar to those of homopolymer **2a** reported previously,[11a] certain $^1$H NMR signals in **2b–l** and **3–7** appeared at higher field and with significant broadening relative to those of the corresponding monomers **1**. Presumably, the anisotropic shielding arising from the adjacent porphyrin moiety may be responsible for such shifts. The $^1$H NMR signals of the porphyrin pendants with amidic alanine linkers (polymers **2c–f**) were much broader than those without hydrogen bonded linkers. Apparently, hydrogen bonding between pendants would make the polymers more rigid, leading to broader signals in the $^1$H NMR spectra. Similar behavior was found in rigid double-stranded ladderphanes with porphyrin linkers.[18c]

It is interesting to note that the chemical shifts of α-methylene (next to the oxygen atom) protons on the *para*-alkoxy substituents of the two phenyl groups at the $C^{10}$ and $C^{20}$ positions were very sensitive to hydrogen bonding in the pendants. They appeared at $\delta = 3.12$, 3.81, and 3.93 ppm for **2d** (with two hydrogen bonds per monomeric unit), **2h** (with one hydrogen bond per monomeric unit), and **2j** (no hydrogen bonds), respectively. Hydrogen bonding might bring two adjacent porphyrin pendants closer so that the relevant protons appeared at higher field owing to the anisotropic shielding. However, the chemical shift of similar α-methylene protons on the phenyl substituent at $C^{15}$ was less sensitive. The ratios of monomeric units with zinc–porphyrin and free base porphyrin pendants in **3–7** were determined by integration of the N–H protons in the pyrrole rings ($\delta =$




Scheme 1. a) Boc-alanine (**8L** or **8D**), EDCI/DMAP, 95% for both **10L** and **10D**; b) TFA, 98% for **11L** and 93% for **11D**; c) $(COCl)_2$; d) **13**, $Et_3N$, 90% for **1d** and 92% for **1f**; e) **13**, $Et_3N$, 85%; f) LiOH, THF/$H_2O$ (10:3), 85%; f) **9** or **16**, EDCI/DMAP, 95% for **1h** and 90% for **1j**; h) $Zn(OAc)_2$, 94% for **1c**, 91% for **1e**, 91% for **1g**, and 97% for **1i**; i) $[Cl_2(Cy_3P)_2Ru{=}CHPh]$, 96% for **2c**, 99% for **2d**, 95% for **2e**, 93% for **2f**, 90% for **2g**, 98% for **2h**, 87% for **2i**, 95% for **2j**, 85% for **3** ($m/n$ = 1.5:1), 93% for **4** ($m/n$ = 1:1), 98% for **5** ($m/n$ = 1:1), 93% for **6** ($m/n$ = 1:1), 92% for **7** ($m/n$ = 1:1).

−2.8 ppm) and the protons at the β positions (around $\delta$ = 8.8 ppm) in the $^1$H NMR spectra.

Dimers **16** and **17** were synthesized to compare the helicity of the polymers **2c–f** (Scheme 2). The observation of two nonequivalent sets of the $^{13}$C NMR signals for the two ring-opened norbornene moieties in **23** indicates that the molecule may adopt $C_1$ symmetry and therefore have isotactic stereochemistry with *trans* double bonds and the two pendants in *syn* conformation.[14c] Since further transformations of **23** into **16** and **17** may not affect the stereochemistry of the double bonds and the asymmetric centers, it seems reasonable to suggest that both **16** and **17** may have similar stereochemistry to that of **23**.

## Photophysical Properties

Homopolymers **2**: The photophysical properties of monomers **1** and homopolymers **2a–l** are also outlined in Table 1. The absorption spectra of **1c**,**d**,**g–i** and **2c**,**d**,**g–i** are shown in Figure 1 and the absorption spectra of the rest of monomers and polymers together with the emission spectra of **1** and **2** are included in Figures S1 and S2 in the Supporting Information. As described previously,[11a] the Soret band of polymers **2a**,**b** showed neither splitting nor bathochromic shifts relative to those of the corresponding monomers **1a** and **1b**. Polymers **2i–l** behaved similarly. In contrast, when the alanine linker was employed, a shoulder was observed in the Soret band at 410 nm for polymers with free base porphyrin pendants **2d** and **2f**. In addition, significant broadening of the Soret band was observed for **2c** and **2e**. Presumably, exciton coupling between the adjacent pending porphyrins may occur in these homopolymers. These polymers have the bisamidic alanine linkers between the porphyrin chromophores and the PNB backbone. As mentioned earlier, the span occupied by each of the monomers would be around 5.5 Å.[15b] It seems likely that hydrogen bonding between the adjacent bisamidic chiral alanine moieties in these polymers may play an important role to bring the porphyrin chromophores to more suitable orientation for exciton coupling. Even with monoamidic L-lactate linkers (polymers **2g** and **2h**), in which only one hydrogen bond is available for each of these linkers, the Soret bands of their polymers were somewhat broader than those of the corresponding monomers **1g** and **1h**.

The Q-band absorptions of zinc–porphyrin-appended polymers **2c**, **2e**, and **2g** also appear to be slightly sensitive to hydrogen bonding in the linkers. For example, **2c** and **2e** absorb at 557 and 600 nm, whereas the corresponding monomers **1c** and **1e** exhibit absorption maxima at 551 and 591 nm. The Q-band absorptions for **2g** (554 and 598 nm) also exhibit a slight red shift relative to those of **1g** (551 and 592 nm).

As can been see from Table 1, the $\lambda_{em}$ bands for free base porphyrin-appended PNBs **2** are almost the same as those for the corresponding monomers **1**. Intriguingly, the emission maxima of polymers **2c** and **2e** showed bathochromic shifts (11 nm) relative to the emission of the corresponding monomers **1c** and **1e**. The shifts became less prominent for polymers **2g** and **2i** relative to **1g** and **1i**, respectively. Furthermore, the decrease of quantum yields from monomers to polymers also depends on the nature of the linkers. Thus, the quantum yields for zinc–porphyrin-appended polymers **2c** and **2e** were significantly lower than those of **1c** and **1e**, respectively. The quantum yield of polymer **2i** appeared to be affected much less than that of **1i**. Again, hydrogen bonding will bring the two adjacent porphyrins closer so that interactions between these chromophores may lead to a red shift in their emission profiles and a reduction in quantum yields.

Random copolymers **3–7**: The photophysical properties of random copolymers **3–7** are also tabulated in Table 1 and the absorption of these polymers are shown in the Supporting Information (Figure S3). The Q bands were essentially a superposition of the spectra of a mixture of the corresponding monomeric zinc–porphyrin and the free base porphyrin components of same ratios. It is interesting that the full width at half maximum (fwhm) values of the Soret band for random copolymers **4–6** decreased with the availability of hydrogen bonding in the linkers (Table 1).

The emission profiles of random copolymers **3–7** and of a mixture of the corresponding homopolymers **2** of same

Table 1. Photophysical properties of **1**–**7**.

| Compd | $M_n$ (PDI) | Soret band[a,b] $\lambda_{max}$ [nm] (log ε) | Q-bands[a] $\lambda_{max}$ [nm] (log ε) | Emission $\lambda_{max}$ [nm][c] | $\Phi_f$[d] | Lifetime $\tau$ [ps] (rel. wt.)[e] | $\eta$ |
|---|---|---|---|---|---|---|---|
| **1b** | – | 421 (5.65) [790] | 518 (4.19), 554 (4.08), 593 (3.73), 650 (3.73) | 656 | 0.033 | 8400 | – |
| **2b** | 28367 (1.40) | 422 (5.50) [1129] | 518 (4.17), 555 (4.05), 592 (3.70), 650 (3.70) | 658 | 0.030 | 860 (17%) 8400 (83%) | – |
| **1d** | – | 422 (5.54) [845] | 518 (4.00), 556 (3.86), 594 (3.52), 650 (3.58) | 655 | 0.037 | 8450 | – |
| **2d** | 14820 (1.11) | 423 (5.27) [1658] | 520 (4.04), 557 (3.90), 595 (3.55), 651 (3.55) | 656 | 0.030 | 480 (52%), 8450 (48%) | – |
| **1f** | – | 422 (5.54) [846] | 518 (4.01), 554 (3.87), 592 (3.52), 650 (3.56) | 655 | 0.036 | 8600 | – |
| **2f** | 11460 (1.11) | 423 (5.26) [1653] | 520 (4.03), 557 (3.90), 595 (3.53), 651 (3.55) | 656 | 0.029 | 560 (57%), 8600 (43%) | – |
| **1h** | – | 422 (5.66) [730] | 519 (4.22), 556 (4.08), 595 (3.74), 651 (3.81) | 654 | 0.028 | 8420 | – |
| **2h** | 17600 (1.09) | 422 (5.54) [1038] | 519 (4.25), 557 (4.10), 595 (3.77), 650 (3.80) | 655 | 0.021 | 1300 (34%), 8400 (66%) | – |
| **1j** | – | 422 (5.55) [734] | 518 (4.12), 555 (3.94), 594 (3.60), 650 (3.64) | 656 | 0.031 | 8800 | – |
| **2j** | 16490 (1.19) | 422 (5.48) [957] | 519 (4.15), 556 (3.97), 595 (3.63), 651 (3.63) | 656 | 0.029 | 2400 (21%), 8800 (79%) | – |
| **1l** | – | 418 (5.49) [659] | 518 (4.15), 554 (3.95), 598 (3.60), 655 (3.78) | 656, 714 | 0.015 | 8450 | |
| **2l** | 11000 (1.13) | 418 (5.34) [1033] | 519 (4.04), 555 (3.85), 599 (3.48), 656 (3.70) | 658, 716 | 0.012 | 2200 (24%) 8450 (76%) | |
| **1a** | – | 423 (5.68) [841] | 550 (4.34), 589 (3.91) | 602 | 0.040 | 1340 | |
| **2a** | 34200 (1.50) | 423 (5.52) [1225] | 552 (4.31), 592 (3.89) | 610 | 0.025 | 228 (72%), 1350 (28%) | |
| **1c** | – | 423 (5.67) [669] | 551 (4.27), 591 (3.81) | 600 | 0.029 | 1650 | – |
| **2c** | 14190 (1.13) | 425 (5.36) [1486] | 557 (4.17), 600 (3.87) | 611 | 0.009 | 230 (73%), 1650 (27%) | – |
| **1e** | – | 423 (5.66) [669] | 551 (4.28), 591 (3.81) | 600 | 0.030 | 1600 | – |
| **2e** | 13670 (1.13) | 424 (5.37) [1485] | 557 (4.18), 600 (3.87) | 611 | 0.009 | 215 (79%), 1600 (21%) | – |
| **1g** | – | 423 (5.74) [669] | 551 (4.35), 592 (3.91) | 600 | 0.029 | 1510 | – |
| **2g** | 15500 (1.12) | 424 (5.51) [1188] | 554 (4.28), 598 (3.93) | 604 | 0.017 | 190 (66%), 1510 (34%) | – |
| **1i** | – | 423 (5.59) [700] | 551 (4.19), 591 (3.69) | 601 | 0.030 | 1340 | – |
| **2i** | 12760 (1.14) | 424 (5.49) [919] | 552 (4.18), 592 (3.72) | 604 | 0.022 | 221 (45%), 1340 (55%) | – |
| **1k** | – | 420 (5.51) [613] | 554 (4.15), 593 (3.78) | 600 | 0.036 | 1420 | – |
| **2k** | 17000 (1.19) | 407 (5.19), 420 (5.29) [1749] | 557 (4.08), 596 (3.78) | 605 | 0.007 | 182 (72%), 1420 (28%) | – |
| **3** | 14390 (1.12) | 422 (5.51) [1124] | 518 (3.90), 553 (4.15), 593 (3.78), 651 (3.30) | 613, 663 | 0.018 | 43 (35%), 207 (53%), 1350 (12%) | 0.47 |
| **4** | 13400 (1.11) | 423 (5.31) [1477] | 520 (3.90), 557 (4.04), 598 (3.70), 651 (3.30) | 612, 661 | 0.021 | 29 (87%), 202 (10%), 1600 (3%) | 0.85 |
| **5** | 18000 (1.12) | 423 (5.54) [1110] | 520 (4.04), 556 (4.20), 597 (3.85), 651 (3.48) | 603, 654, 710 | 0.018 | 40 (53%), 270 (43%), 1510 (4%) | 0.69 |
| **6** | 17500 (1.11) | 423 (5.54) [953] | 518 (4.00), 553 (4.18), 593 (3.78), 650 (3.48) | 602, 654, 711 | 0.017 | 58 (11%), 242 (55%), 1340 (34%) | 0.21 |
| **7** | 11600 (1.24) | 419 (5.20) [1330] | 520 (3.78), 556 (3.85), 599 (3.48), 656 (3.30) | 604, 657, 717 | 0.007 | 50 (45%), 182 (42%), 1420 (13%) | 0.46 |

[a] Molar extinction coefficients (log[$M^{-1}cm^{-1}$]), based on the molecular weight of the monomeric unit, are shown in parentheses. [b] Numbers in square bracket are the fwhm values ($cm^{-1}$) of the Soret band. [c] Excitation at $\lambda_{ex}=550$ nm. [d] With reference to [Zn(TPP)] in toluene ($\Phi_f=0.033$). [e] Relative weights were fitted based on the formula $\Sigma\alpha_i \exp(-t/\tau_i)$.

ratios are compared in the Supporting Information (Figure S4). In these random copolymers **3**–**7**, the relative intensities of the emission around 600–610 nm, attributed to the emission of the zinc–porphyrin complex, were much lower than those of the luminescence around 654–660 nm arising from the emission of the free base porphyrin, where the fluorescence intensities of these two chromophores were comparable in the mixture of homopolymers. Again, the relative intensities of the emission around 600 nm and 655 nm in **4**–**6** appeared to be dependent on the number of hydrogen bonds between adjacent pendants. Since there were no changes in emission wavelength in these two systems, these results suggest that FRET from zinc–porphyrin to free base porphyrin might occur.

### Time-Resolved Fluorescence Spectroscopy

A femtosecond laser equipped with a streak camera was employed to measure the time-resolved fluorescence spectra of monomers **1**, polymers **2**, and copolymers **3**–**7** in $CH_2Cl_2$. The emission at 590–610 nm was monitored, and the decay curves are shown in the Supporting Information (Figure S5).

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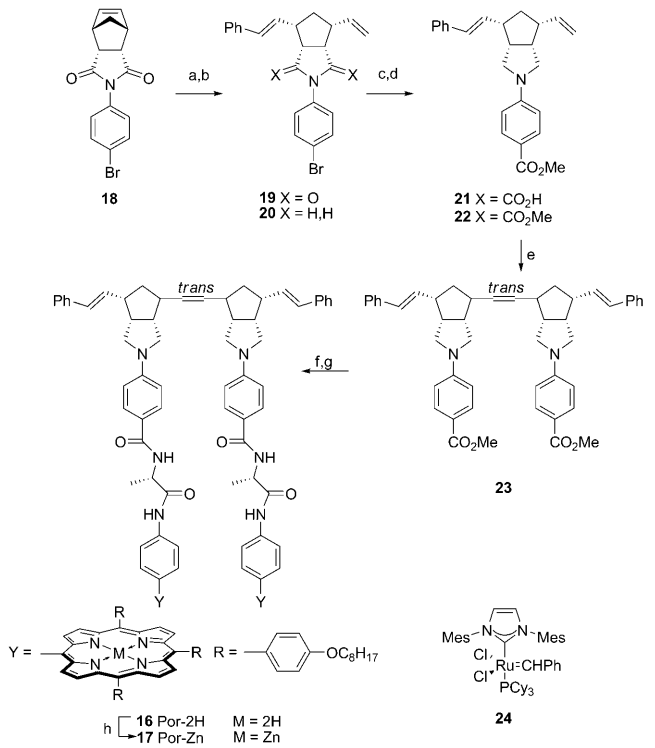


Scheme 2. a) [PhCH=$CH_2$, $Cl_2(PCy_3)_2$Ru=CHPh], 75%; b) LAH, 84%; c) (i) *n*BuLi, $CO_2$(g), 71%; d) $(COCl)_2$, then MeOH, 92%; e) **24**, 28%; f) NaOH, MeOH/THF; g) $(COCl)_2$, then **11**. $Et_3N$, 72% in two steps; h) $Zn(OAc)_2$, 89%.

The lifetimes of **1**–**7** obtained by fitting are also summarized in Table 1.

Multiexponential fitting ($\Sigma\,\alpha_i \exp(-t/\tau_i)$ was utilized to resolve two decay lifetimes for homopolymers **2** and three decay lifetimes for copolymers **3**–**7**. The amplitude-weighted lifetimes ($\tau_{DA}$) were calculated from a summation of the products of the lifetimes ($\tau_i$) and the amplitudes ($\alpha_i$) observed for copolymers **3**–**7**, and $\tau_D$ values were obtained similarly for homopolymers **2** [Eq. (1)]. The efficiencies of energy transfer ($\eta$) were estimated according to Equation (2).[27]

$$\tau_D \text{ (or } \tau_{DA}) = \Sigma\alpha_i\tau_i \quad (1)$$

$$\eta = 1-(\tau_{DA}/\tau_D) \quad (2)$$

As shown in Table 1, three components of the fluorescence decay lifetimes were involved in the observed fluorescence decay signal from the zinc–porphyrin moiety in copolymers **3**–**7**. The long decay lifetimes (larger than 1000 ps) were assigned to the intrinsic fluorescence lifetimes for the emission of the zinc–porphyrin chromophore. The shorter lifetimes (less than 100 ps) might be mainly from FRET between the donor zinc–porphyrin and the acceptor free base porphyrin. It is noteworthy that the fluorescence lifetimes ranging from 200 to 270 ps in random copolymers **3**–**7** fall within the same range as that for self-quenching between adjacent chromophores in homopolymers **2**. Different weightings of each component were contributed by the competition among FRET, self-quenching, and intrinsic emission [Eq. (1)].[28] The energy transfer efficiencies ($\eta$) for FRET were calculated accordingly [(Eq. (2)].

As can be seen from Table 1, the relative weighting of the shorter lifetime in copolymer **4** was higher than that in **5**, which in turn was higher than that in **6**. As mentioned before, the diamidic alanine linker in each pendant in **4** would form two hydrogen bonds with the next adjacent pendant. Such hydrogen bonding would bring two adjacent pending chromophores to more suitable orientation for interactions. Consequently, when a zinc–porphyrin and a free base porphyrin are well oriented next to each other, more efficient FRET might be expected.

As described earlier, all pendants of PNBs **2**–**7** may be essentially aligned in a similar direction. Nevertheless, the adjacent pendants would not be in the eclipsed conformation, but rather in a gauche conformation like that of an ethane molecule.[15] The dihedral angle between adjacent pendants would depend on the nature of interactions between these moieties. Thus, the distance between the adjacent appended chromophores would be controlled. The lengths of the pendants for **4**–**6** were similar. The energy transfer efficiency, $\eta$, for **4** was higher than that for **5**, which, in turn, was even higher than that for **6**. The presence of hydrogen bonding would better orientate adjacent chromophores so that $\eta$ would be enhanced. In addition, the $\eta$ values for **3** and **7** were somewhat higher than that of **6**, in which all pendant groups in these copolymers are not involved in hydrogen bonding. Since the pendants in **3** and **7** were shorter than that of **6**, more efficient energy transfer would be expected because the interactions between the adjacent chromophores in **3** and **7** might be somewhat better than those in **6**.

### Helicity and Hydrogen Bonding

Homopolymers **2c–h**: As described above, hydrogen bonding between the amidic linkers in copolymers **4** and **5** brings the pending porphyrin chromophore into a more suitable orientation for interactions so that FRET becomes more efficient than in those systems without hydrogen bonding (e.g., **3**, **6**, and **7**). In this study, both D- and L-alanines were used as linkers in homopolymers **2c–f** and copolymer **4**. The incorporation of amino acid pendants onto a polymer may induce the helicity of the polymer.[9] Accordingly, **2c–f** were subject to circular dichroism (CD) measurements (Figure 2). The CD properties of **2g** and **2h** are also shown in Figure 2 for comparison. In comparison, the CD curves for monomers **1c–j** were very weak (Supporting Information, Figure S6).

Homopolymers with zinc–porphyrin pendants (**2c** and **2e**) and with free base porphyrin pendants (**2d** and **2f**) exhibited mirror image CD curves with very prominent intensities in the Soret band region. The Cotton effect in this Soret band region appeared to be opposite to that of the shorter

  

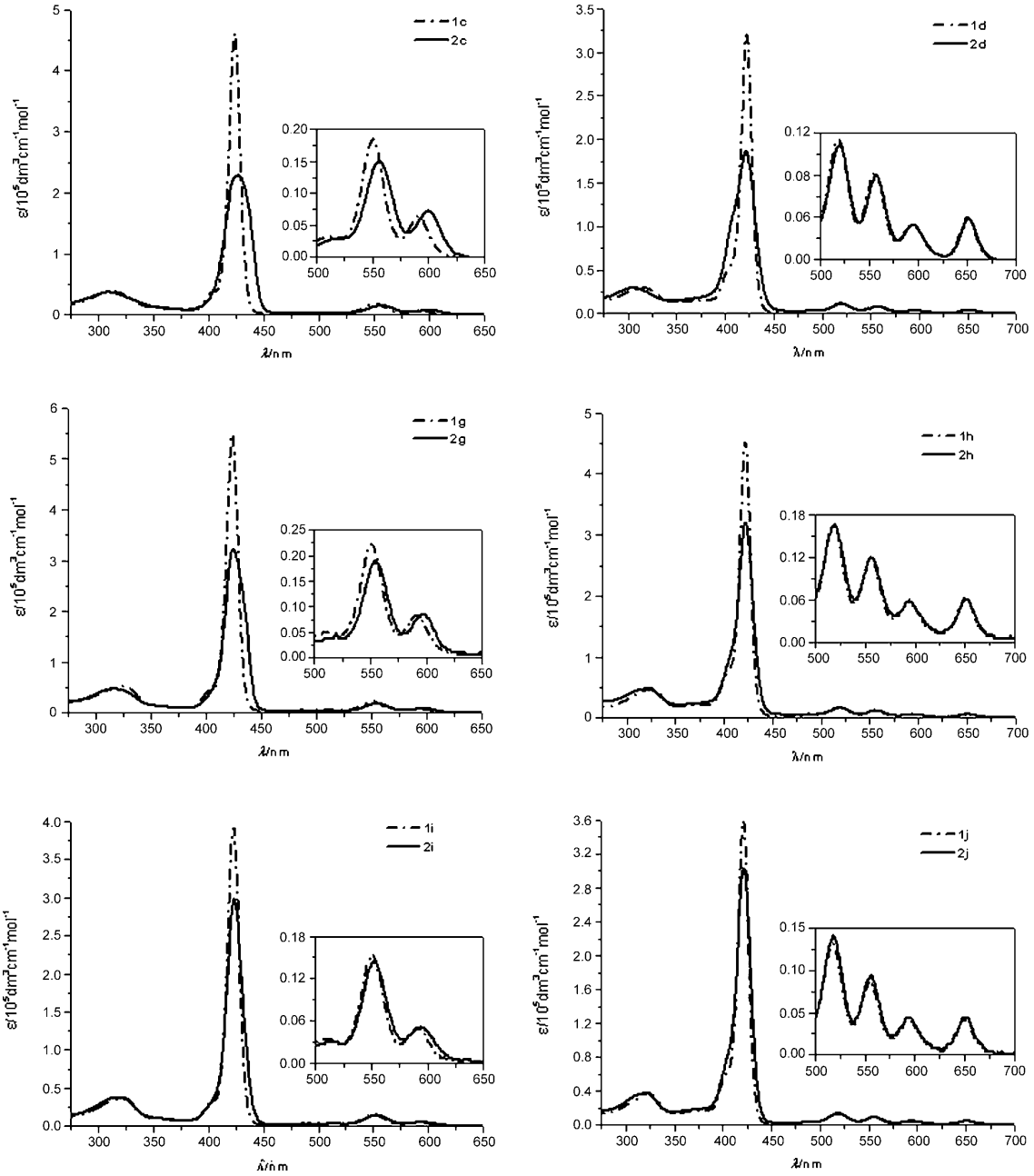


Figure 1. Absorption spectra of **1c**,**d**,**g**–**j** and **2c**,**d**,**g**–**j** in $CH_2Cl_2$.

wavelength region (280–330 nm) for the absorption of the aminobenzamide chromophores. Similar behavior was found in substituted polyacetylenes.[9] The intensities of the CD curves of **2c** and **2d** slightly decreased with increasing temperature and were recovered upon cooling to ambient temperature (Supporting Information; Figure S7 a,b). The fwhm and $\lambda_{max}$ values remain essentially unchanged with variation of the temperature. These results suggest that polymers **2c**–**f** may adopt single-handed helical structures and significant exciton coupling between orderly oriented adjacent porphyrin chromophores might take place. A strong CD response of **2c**–**f** suggests that these polymers, like other related PNBs reported earlier,[15] may adopt homogeneous tacticity and that all double bonds would be in *trans* configuration.

The helicity of the polymers **2c**–**f** can be understood within the framework of the exciton chirality method.[28] In other words, the exciton coupling between the appended porphyrins and aminobenzamide moieties would be responsible for the helicity of the complexes. Since the porphyrin moiety has a much higher extinction coefficient than that of the aminobenzamide group, the intensity of the CD curves at 360–460 nm was much higher than that around 300 nm. In addition, the exciton couplet amplitudes among these polymers would be related to the interchromophore distance as

  

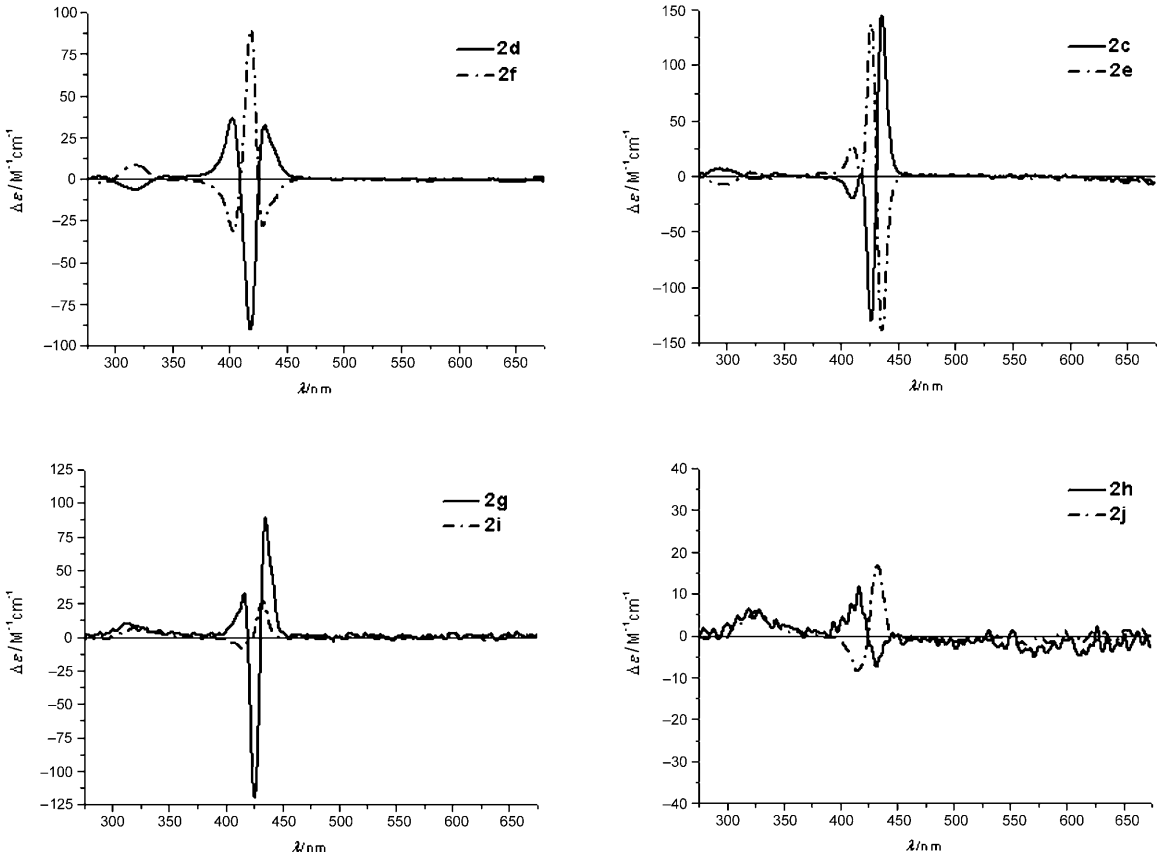


Figure 2. CD curves of homopolymers **2c**–**j** in $CH_2Cl_2$.

well as the dihedral angle of the interacting moments. As mentioned earlier, all pendants in **2**–**7** would align coherently towards the same direction, and the spacing occupied by each of the monomeric units in PNBs would be about 0.5–0.6 nm.[11a,14] The dihedral angle of the interacting chromophores would likely offer a platform to dictate the intensity of the couplet. The Δε value could therefore be estimated by the summation of the contribution from each interacting pair of these complexes. The uniformity of the orientation of these interacting chromophores in these complexes would determine the amplitude of the CD curves.

As shown in Figure 2, the intensity of the CD curve for **2g** with zinc–porphyrin pendants was similar to those of **2c**. The temperature dependent CD profile for **2g** is also shown in the Supporting Information (Figure S7c). In contrast to the cases of **2c** and **2d**, the intensities decreased more significantly as temperature increased with more than 80% reduction at 80°C. Since there is only one hydrogen bond between adjacent lactamide linkers, it seems likely that **2g** might be easier to be "denatured" to give disordered structure, which would be CD-inactive.

Surprisingly, the CD intensity for **2h** with the free base porphyrin pendants was low. Polymers **2h** exhibited an opposite Cotton effect to that of **2d**. Polymers **2i** and **2j**, having the lactate linker without hydrogen bonding between adjacent pendants, exhibited very low CD intensities with the same Cotton effect as that of **2c** and **2d**. Even in the presence of chiral linkers, simple π–π interactions between adjacent pendants might not lead to single-handed helicity of the polymer. Increases in the fwhm values of the Soret bands of **2h**–**j**, relative to the corresponding monomers **1h**–**j**, were much less than those of other homopolymer analogues shown in Table 1. Presumably, the exciton coupling would be relatively weak, and, hence, the CD intensities were comparatively low.

Dimers **16** and **17**: Dimers **16** and **17** were subject to CD measurements to verify the nature of the exciton coupling between adjacent chromophores in polymers (Figure 3). The absorption and emission spectra of **16** and **17** (Figure S8 in the Supporting Information) were comparable to those of the corresponding monomers **1d** and **1c** and of the corresponding polymers **2d** and **2c**, respectively. The CD curves for **16** and **17** showed similar Cotton effects in the aminobenzamide absorption region (300–350 nm) as those for **2d** and **2c**, respectively. Both **16** and **17** exhibited strong CD response in the Soret band region, but, surprisingly, opposite Cotton effects to those for **2d** and **2c**.

Density functional theory (DFT) calculations were carried out to examine the possible conformation of model dimer **25** containing two additional alanine-based units to avoid intrapendant hydrogen bonding between the two amidic species. The optimized geometries of **25** are shown in Figure 4.

  

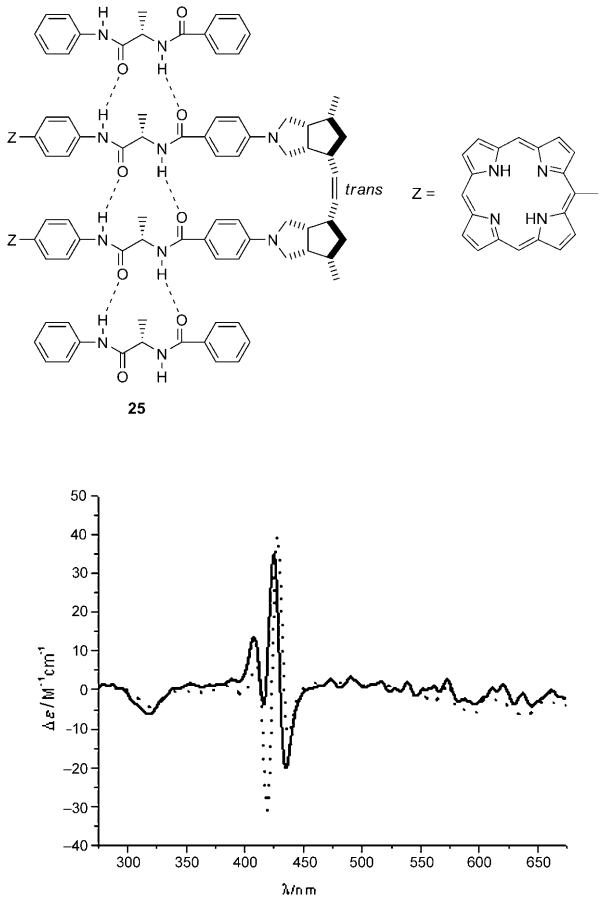


Figure 3. CD curves of **16** (solid) and **17** (dotted) in $CH_2Cl_2$.

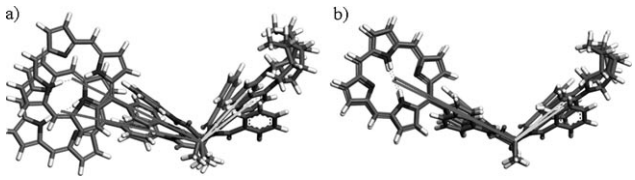


Figure 4. DFT-calculated structures of **25** in a) helical form (torsional angles 13° and 10°) and b) sheet form (torsional angles 1° and 4°).

The helix form was found to be 5.2 kcal mol$^{-1}$ more stable than the sheet form. The two adjacent alanine moieties form hydrogen bonds with an average distance around 2 Å. For the helix form, the projected torsional angle of two pendants defined by two lines from the chiral center of the alanine and the center of the porphyrin was 13° with right-handed rotation. The two lines defined from the chiral center of the amino acid and the center of the aminobenzamide moiety for the helix form also yielded a right-handed torsional angle of 10°. These right-handed rotations for torsional angles described above are consistent with the negative Cotton effect in the CD spectrum for **16** shown in Figure 3.

The discrepancy of the Cotton effect between dimers **16**, **17**, and polymers **2c–f** is striking. It is known that π–π interactions between porphyrin rings are strong.[29] The mode of packing in polymers such as **2c–f** and those in dimers **16** and **17** might be different. Nevertheless, the present results indicate that there might be strong exciton coupling between adjacent porphyrin pendants in these dimers and polymers leading to a strong CD response.

Random copolymers **4–6**: The CD profiles of **4–6** are shown in Figure 5. Again, copolymer **4** having two hydrogen

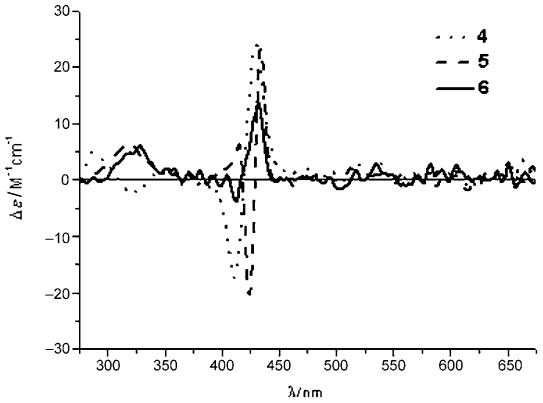


Figure 5. CD curves of **4–6** in $CH_2Cl_2$.

bonds between the adjacent pendants exhibited a fairly strong CD response with the same Cotton effect as that of the corresponding homopolymers **2c** and **2d**. Copolymer **5** containing only one hydrogen bond between adjacent pendants behaved similarly. However, the shape of the CD profile of **5** was somewhat different from that of **4**, while both copolymers showed similar absorption spectra. When a lactate was employed as the linker through the ester bonds for **6**, the CD intensity was relatively weak.

## Conclusions

In summary, we have addressed an interesting feature on the nature of linkers on the photophysical properties of porphyrin-appended PNBs. The use of bisamidic chiral alanine linkers between the pending porphyrins and the polymeric backbone has been shown to bring the adjacent porphyrin chromophores to more suitable orientation for exciton coupling because of hydrogen bonding between adjacent linkers. The hydrogen bonds between the adjacent pendants in these polymers may induce a cooperative effect and therefore render single-handed helical structures for these polymers (e.g., **2c–f**). Such a cooperative effect is reflected in the enhancement of FRET efficiencies between the zinc–porphyrin and free base porphyrin in the random copolymers **4** and **5**.

## Experimental Section

**General**: Gel permeation chromatography (GPC) was performed on a Waters GPC machine with an isocratic HPLC pump (1515) and a refractive index detector (2414). THF was used as the eluent (flow rate =

  

1.0 mL min$^{-1}$). Waters Styragel HR2, HR3, and HR4 columns (7.8× 300 mm) were employed for determination of relative molecular weight using polystyrene as standard ($M_n$ values ranged from 375 to $3.5\times10^6$). Absorption spectra were measured on a Hitachi U-3310 spectrophotometer and emission spectra on a Hitachi F-4600 fluorescence spectrophotometer. Quantum yield was obtained using ZnTPP (TPP = tetraphenylporphyrin) in toluene as the reference ($\Phi = 0.033$). CD spectra were recorded on a JASCO J-815 spectropolarimeter.

**Compound 10L**: To a solution of **9**[11a] (507 mg, 0.5 mmol) in $CH_2Cl_2$ (50 mL) were added sequentially *Boc*-L-alanine (113 mg, 0.6 mmol; Boc = *tert*-butyloxycarbonyl) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI) (115 mg, 0.6 mmol) and a catalytic amount of 4-methylaminopyridine (DMAP; 7 mg, 0.06 mmol), and the mixture was stirred at room temperature overnight. The mixture was washed with water (100 mL) and brine (100 mL). The organic phase was evaporated in vacuo to give the residue, which was purified by chromatography (silica gel, $CH_2Cl_2/CH_3OH = 100:1$, v/v) to give **10L** as a purple solid (570 mg, 95%): m.p.: 201–202°C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta = -2.78$ (s, 2H; NH), 0.95 (t, $^3J$ (H,H) = 6.3 Hz, 9H), 1.35–1.50 (m, 24H), 1.50–1.70 (m, 18H), 1.87–1.99 (m, 6H), 3.97 (br, 4H), 4.23 (t, $^3J$ (H,H) = 6.3 Hz, 2H), 4.59 (br, 1H), 5.27 (br, 1H), 6.79 (d, $^3J$ (H,H) = 7.2 Hz, 2H), 7.04 (d, $^3J$ (H,H) = 7.2 Hz, 2H), 7.26 (d, $^3J$ (H,H) = 7.2 Hz, 2H), 7.64 (d, $^3J$ (H,H) = 7.2 Hz, 2H), 7.86 (d, $^3J$ (H,H) = 7.2 Hz, 2H), 7.97 (d, $^3J$ (H,H) = 7.2 Hz, 2H), 8.10 (d, $^3J$ (H,H) = 7.2 Hz, 2H), 8.18 (d, $^3J$ (H,H) = 7.2 Hz, 2H), 8.63 (s, 2H; β-H), 8.79–8.85 (m, 6H; β-H), 9.15 ppm (s, 1H; CONH); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 14.2$, 17.4, 22.7, 26.2, 28.4, 29.3, 29.5, 31.9, 51.2, 53.4, 68.21, 68.3, 80.9, 112.5, 112.60, 112.69, 118.0, 119.1, 119.8, 120.0, 130.9 (br), 134.3, 134.4, 135.1, 135.5, 135.6, 137.6, 138.2, 158.9, 159.0, 173.9 ppm; IR (KBr): $\tilde{\nu} = 3317$, 2928, 2856, 1683, 1606, 1509, 1469, 1351, 1287, 1245, 1174, 966, 802, 738 cm$^{-1}$; HRMS (MALDI): *m*/*z*: calcd for 1185.7185 ($C_{76}H_{93}N_6O_6$, [$M^+$+H]); found: 1185.7151.

In a similar manner, **10D** was obtained in 95% yield from **9** (710 mg, 0.7 mmol) and *Boc*-D-alanine (159 mg, 0.84 mmol); HRMS (MALDI): *m*/*z*: calcd for 1184.7030 ($C_{76}H_{92}N_6O_6$, [$M^+$]); found: 1184.7073.

**Compound 11L.** A mixture of **10L** (474 mg, 0.4 mmol) and trifluoroacetic acid (TFA; 10 mL) in $CH_2Cl_2$ (40 mL) was stirred for 2 h. After evaporation of the solvent and TFA in vacuo, the residue was dissolved in $CH_2Cl_2$ (50 mL) and washed with an aqueous 10% sodium bicarbonate solution (50 mL), water (100 mL), and brine (100 mL). The organic phase was evaporated in vacuo and the residue was chromatographed on silica gel ($CH_2Cl_2/CH_3OH = 25$: 1, v/v) to give **11L** as a purple solid (425 mg, 98%): m.p.: 221–223°C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta = -2.77$ (s, 2H; NH), 0.93 (t, $^3J$ (H,H) = 6.3 Hz, 9H), 1.35–1.50 (m, 24H), 1.50–1.57 (m, 9H), 1.90–2.20 (m, 8H), 3.70–3.90 (m, 1H), 4.12 (t, $^3J$ (H,H) = 6.3 Hz, 4H), 4.20 (t, $^3J$ (H,H) = 6.3 Hz, 2H), 7.16–7.26 (m, 6H), 7.98–8.07 (m, 6H), 8.10 (d, $^3J$ (H,H) = 8.4 Hz, 2H), 8.18 (d, $^3J$ (H,H) = 8.4 Hz, 2H), 8.84–8.86 (m, 8H; β-H), 9.90 ppm (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 14.2$, 21.6, 22.7, 26.2, 29.3, 29.5, 31.9, 51.2, 68.2, 112.6, 117.6, 119.3, 119.9, 120.0, 130–132 (br), 134.3, 134.4, 135.1, 135.5, 135.6, 137.5, 138.0, 158.90, 158.92, 173.9 ppm; IR (KBr): $\tilde{\nu} = 3313$, 2924, 2853, 1693, 1606, 1519, 1506, 1468, 1402, 1349, 1284, 1244, 1174, 1101, 966, 801, 735 cm$^{-1}$; HRMS (MALDI): *m*/*z*: calcd for 1085.6646 ($C_{71}H_{85}N_6O_4$, [$M^+$+H]); found: 1085.6627.

In a similar manner, **11D** was obtained in 93% yield from **10D** (780 mg, 0.65 mmol) and TFA (25 mL); HRMS (MALDI): *m*/*z*: calcd for 1085.6636 ($C_{71}H_{85}N_6O_4$, [$M^+$+H]); found: 1085.6627; elemental analysis calcd (%) for $C_{71}H_{84}N_6O_4$: C 78.56, H 7.80, N 7.74; found: C 78.13, H 7.83, N 7.62.

**Compounds 1d and 1f**: To a solution of **12** (115 mg, 0.45 mmol) in $CH_2Cl_2$ (10 mL) at 0°C was added oxalyl chloride (0.13 mL, 1.5 mmol). The mixture was gradually warmed to room temperature and stirred for 30 min. The solvent was removed in vacuo to give the corresponding acid chloride, which was used for the next reaction without further purification. To a $CH_2Cl_2$ (10 mL) solution of **11L** (326 mg, 0.3 mmol) and triethylamine (0.05 mL, 0.45 mmol) cooled to 0°C under argon was added dropwise a solution of the freshly prepared acid chloride described above in $CH_2Cl_2$ (5 mL). The mixture was allowed to warm to room temperature and stirred for an additional 4 h. After evaporation of the solvent and triethylamine in vacuo, the residue was purified by column chromatography (silica gel, $CH_2Cl_2/CH_3OH = 100:1$, v/v), to give a purple solid **1d** (350 mg, 90%): m.p.: 156–157°C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta = -2.78$ (s, 2H), 0.92 (t, $^3J$ (H,H) = 6.5 Hz, 9H), 1.35–1.49 (m, 24H), 1.52–1.62 (m, 8H), 1.71 (d, $^3J$ (H,H) = 7.1 Hz, 3H), 1.91–2.00 (m, 6H), 2.93–2.95 (m, 4H), 3.04–3.06 (m, 2H), 3.24–3.28 (m, 2H), 4.17 (t, $^3J$ (H,H) = 6.5 Hz, 4H), 4.23 (t, $^3J$ (H,H) = 6.5 Hz, 2H), 5.10 (quint, $^3J$ (H,H) = 7.1 Hz, 1H), 6.13 (s, 2H), 6.43 (d, $^3J$ (H,H) = 8.9 Hz, 2H), 6.61 (d, $^3J$ (H,H) = 7.2 Hz, 1H), 7.15 (d, $^3J$ (H,H) = 8.1 Hz, 2H), 7.18 (d, $^3J$ (H,H) = 8.1 Hz, 2H), 7.25 (d, $^3J$ (H,H) = 8.4 Hz, 2H), 7.77 (d, $^3J$ (H,H) = 8.9 Hz, 2H), 7.97 (d, $^3J$ (H,H) = 8.4 Hz, 2H), 7.99 (d, $^3J$ (H,H) = 8.1 Hz, 2H), 8.01 (d, $^3J$ (H,H) = 8.1 Hz, 2H), 8.09 (d, $^3J$ (H,H) = 8.4 Hz, 2H), 8.14 (d, $^3J$ (H,H) = 8.4 Hz, 2H), 8.78–8.85 (m, 8H; β-H), 9.58 ppm (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 14.2$, 18.1, 22.7, 26.21, 26.23, 29.3, 29.46, 29.47, 31.9, 45.3, 46.5, 50.2, 50.4, 52.0, 68.2, 68.3, 111.2, 112.47, 112.52, 112.7, 118.3, 119.1, 119.4, 119.8, 128.8, 130–132 (br), 134.2, 134.4, 135.0, 135.4, 135.6, 135.7, 137.9, 149.9, 158.8, 158.9, 168.2, 171.4 ppm; IR (KBr): $\tilde{\nu} = 3313$, 2924, 2853, 1702, 1606, 1502, 1469, 1401, 1377, 1349, 1284, 1245, 1174, 1108, 966, 801, 734 cm$^{-1}$; MS (MALDI): *m*/*z*: 1322.8 ($C_{87}H_{99}N_7O_5$, [$M^+$+H]); elemental analysis calcd (%) for $C_{87}H_{99}N_7O_5$: C 79.00, H 7.54, N 7.41; found: C 79.12, H 7.78, N 7.10.

Compound **1f** was obtained in a similar manner in 92% yield. HRMS (MALDI): *m*/*z*: calcd for 1322.7807 ($C_{87}H_{100}N_7O_5$, [$M^+$+H]); found: 1322.7780.

**Compound 15**: To a solution of ethyl L-lactate (472 mg, 4 mmol) and triethylamine (202 mg, 2 mmol) in $CH_2Cl_2$ (10 mL) cooled at 0°C under argon was added a $CH_2Cl_2$ solution (5 mL) of **13** freshly prepared from **12** (510 mg, 2 mmol) and oxalyl chloride (1.7 mL, 20 mmol) as described above. The mixture was allowed to warm to room temperature and stirred for an additional 4 h. Solvent and excess $Et_3N$ were removed in vacuo and the residue was chromatographed on silica gel ($CH_2Cl_2$) to give a white solid (603 mg, 85%), which was treated with a solution of lithium hydroxide monohydrate (74 mg, 1.8 mmol) in water (1.5 mL) and THF (5 mL). The mixture was stirred at 0°C for 1.5 h. Removal of THF in vacuo followed by the addition of water (10 mL) gave an aqueous solution, which was acidified to pH 2 to afford **15** as a white powder (445 mg, 85%): m.p.: 185–186°C; $[\alpha]_D = +34.3°$ ($c = 0.40$ M, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.56$ (d, $^2J$ (H,H) = 8.4 Hz, 1H), 1.62 (d, $^3J$ (H,H) = 7.2 Hz, 3H), 1.66 (dt, $^2J$ (H,H) = 8.4 Hz, 1H), 2.90–3.00 (m, 4H), 3.15–3.16 (m, 2H), 3.37–3.42 (m, 2H), 5.29 (q, $^3J$ (H,H) = 7.2 Hz, 1H), 6.20 (s, 2H), 6.59 (d, $^3J$ (H,H) = 8.4 Hz, 2H), 7.93 ppm (d, $^3J$ (H,H) = 8.4 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 17.4$, 45.6, 46.3, 52.8, 68.3, 113.1, 118.2, 131.2, 135.7, 148.4, 165.2, 175.0 ppm; IR (KBr): $\tilde{\nu} = 3056$, 2968, 2942, 2847, 1701, 1603, 1527, 1473, 1451, 1388, 1343, 1302, 1270, 1175, 1106, 1042, 824, 770, 726 cm$^{-1}$; HRMS (EI): *m*/*z*: calcd for 327.1474 ($C_{19}H_{21}NO_4$, [$M^+$]); found: 327.1471.

**Compound 1h**: A mixture of **9** (202 mg, 0.2 mmol), **15** (98 mg, 0.6 mmol), EDCI (115 mg, 0.6 mmol), and DMAP (7 mg, 0.06 mmol) in $CH_2Cl_2$ (20 mL) was stirred overnight and then washed with water (50 mL) and brine (50 mL). The organic phase was dried ($MgSO_4$), filtered, and evaporated in vacuo to give the residue which was purified by column chromatography (silica gel, $CH_2Cl_2$) to give **1h** as a purple solid (250 mg, 95%): m.p.: 209–221°C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta = -2.73$ (s, 2H), 0.96 (t, $^3J$ (H,H) = 7.2 Hz, 9H), 1.37–1.68 (m, 32H), 1.81 (d, $^3J$ (H,H) = 6.4 Hz, 3H), 2.00 (quint, $^3J$ (H,H) = 7.2 Hz, 6H), 3.01–3.04 (m, 4H), 3.10–3.13 (m, 2H), 3.32–3.37 (m, 2H), 4.23–4.27 (m, 6H), 5.77 (q, $^3J$ (H,H) = 6.8 Hz, 1H), 6.19 (t, $^3J$ (H,H) = 1.6 Hz, 2H), 6.49 (d, $^3J$ (H,H) = 8.8 Hz, 2H), 7.25–7.29 (m, 6H), 7.95 (d, $^3J$ (H,H) = 8.8 Hz, 2H), 8.03 (d, $^3J$ (H,H) = 8.8 Hz, 2H), 8.09 (d, $^3J$ (H,H) = 8.4 Hz, 4H), 8.11 (d, $^3J$ (H,H) = 8.4 Hz, 2H), 8.18 (d, $^3J$ (H,H) = 8.4 Hz, 2H), 8.44 (s, 1H), 8.81–8.88 ppm (m, 8H; β-H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta = 14.3$, 18.0, 22.8, 26.3, 28.5, 29.4, 29.6, 32.0, 45.4, 46.7, 50.5, 52.1, 68.3, 70.5, 111.1, 112.6, 114.7, 118.1, 118.9, 119.8, 119.9, 130–132 (br, embodied a sharp peak at 131.5), 134.17, 134.24, 134.9, 135.37, 135.42, 135.6, 136.8, 138.4, 150.7, 158.7, 165.6, 169.3 ppm; IR (KBr): $\tilde{\nu} = 3420$, 3316, 3031, 2930, 2863, 1707, 1675, 1606, 1525, 1514, 1467, 1378, 1347, 1277, 1249, 1176, 1099, 1036, 970, 799, 770, 739 cm$^{-1}$; HRMS (FAB): *m*/*z*: calcd for 1323.7626 ($C_{87}H_{99}N_6O_6$, [$M^+$+H]); found: 1323.7606.

  

**Compound 1j**: In a manner similar to that described for **1h**, **16** (202 mg, 0.2 mmol) and **15** (98 mg, 0.6 mmol) were converted into **1j** as a purple solid (238 mg, 90%): m.p.: 118–120°C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta=-2.75$ (s, 2H), 0.96 (t, $^3J$ (H,H) = 6.8 Hz, 9H), 1.37–1.68 (m, 32H), 1.92 (d, $^3J$ (H,H) = 6.8 Hz, 3H), 2.00 (quint, $^3J$ (H,H) = 6.8 Hz, 6H), 3.02 (br, 4H), 3.11–3.13 (m, 2H), 3.31–3.37 (m, 2H), 4.26 (t, $^3J$ (H,H) = 6.8 Hz, 6H), 5.62 (q, $^3J$ (H,H) = 6.8 Hz, 1H), 6.19 (s, 2H), 6.45 (d, $^3J$ (H,H) = 8.8 Hz, 2H), 7.25–7.29 (m, 6H), 7.53 (d, $^3J$ (H,H) = 8.4 Hz, 2H), 8.03 (d, $^3J$ (H,H) = 8.4 Hz, 2H), 8.10 (d, $^3J$ (H,H) = 8.4 Hz, 6H), 8.20 (d, $^3J$ (H,H) = 8.0 Hz, 2H), 8.81–8.87 ppm (m, 8H, β-H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta=14.3$, 17.4, 22.8, 26.4, 29.4, 29.6, 29.8, 32.0, 45.4, 46.7, 50.5, 52.1, 68.3, 68.7, 110.9, 112.6, 115.1, 118.4, 119.5, 119.9, 120.0, 131.0, 131.6, 134.16, 134.22, 135.1, 135.4, 135.6, 139.9, 150.2, 150.5, 158.8, 166.3, 170.1 ppm; IR (KBr): $\tilde{\nu}=3316$, 3031, 2923, 2847, 1780, 1708, 1606, 1511, 1498, 1467, 1377, 1343, 1274, 1249, 1172, 1100, 970, 802, 739 cm$^{-1}$; HRMS (FAB): *m/z*: calcd for 1324.7466 ($C_{87}H_{98}N_5O_7$, [$M^+$+H]); found: 1324.7471.

**Compounds 1c and 1e**: To a solution of **1d** (132 mg, 0.1 mmol) in chloroform (30 mL) was added a methanolic solution (10 mL) of Zn acetate dihydrate (219 mg, 1 mmol), and the mixture was stirred at room temperature overnight, poured into water, and extracted with chloroform. The chloroform extract was washed three times with water. The solvent was evaporated and the residue was purified by column chromatography (silica gel, $CH_2Cl_2/CH_3OH = 100:1$, v/v) to give a purple solid **1c** (130 mg, 94%): m.p.: 156–158°C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta=0.91$ (t, $^3J$ (H,H) = 6.4 Hz, 9H), 1.35–1.62 (m, 35H), 1.94 (quint, $^3J$ (H,H) = 6.4 Hz, 6H), 2.84 (d, $^3J$ (H,H) = 10.4 Hz, 2H), 2.94 (br, 2H), 3.00–3.01 (m, 2H), 3.12–3.17 (m, 2H), 4.00 (br, 1H; C*H*CO), 4.17–4.22 (m, 6H), 6.10 (s, 2H), 6.17–6.19 (m, 3H), 7.07 (d, $^3J$ (H,H) = 7.2 Hz, 2H), 7.17–7.28 (m, 6H), 7.70 (d, $^3J$ (H,H) = 7.2 Hz, 2H), 8.03 (d, $^3J$ (H,H) = 8.0 Hz, 4H), 8.08 (d, $^3J$ (H,H) = 8.0 Hz, 4H), 8.75 (s, 1H), 8.90–8.94 ppm (m, 8H; β-H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta=14.1$, 17.1, 22.7, 26.2, 29.3, 29.5, 31.9, 45.3, 46.5, 49.2, 50.3, 52.0, 68.2, 110.7, 112.4, 117.6, 117.8, 120.2, 120.6, 120.7, 128.1, 131.7, 131.8, 134.8, 135.2, 135.3, 135.4, 135.7, 137.1, 138.7, 149.6, 150.1, 150.4, 150.5, 158.6, 167.3, 170.4 ppm; IR (KBr): $\tilde{\nu}=2926$, 2854, 1698, 1606, 1525, 1509, 1493, 1473, 1378, 1339, 1245, 1174, 1108, 1068, 998, 797, 720 cm$^{-1}$; HRMS (MALDI): *m/z*, calcd for 1383.6850 ($C_{87}H_{97}N_7O_5Zn$, [$M^+$]); found: 1383.6837.

In a similar manner, reaction of **1f** (132 mg, 0.1 mmol) and a solution of Zn acetate dihydrate (219 mg, 1 mmol) furnished **1e** (125 mg, 91%) as a purple solid: HRMS (MALDI): *m/z*: calcd for 1383.6862 ($C_{87}H_{97}N_7O_5Zn$, [$M^+$]); found: 1383.6837; elemental analysis calcd (%) for $C_{87}H_{97}N_7O_5Zn$: C 75.38, H 7.05, N 7.07; found: C 74.95, H 7.20, N 7.00.

**Compound 1g**: In a manner similar to that described for **1c**, **1h** (132 mg, 0.1 mmol) was converted into **1g** as a purple solid (126 mg, 91%): m.p.: 209–211°C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta=1.00$ (t, $^3J$ (H,H) = 6.8 Hz, 9H), 1.39–1.50 (m, 25H), 1.57–1.65 (m, 10H), 1.95 (quint, $^3J$ (H,H) = 6.8 Hz, 6H), 2.84 (d, $^3J$ (H,H) = 10.4 Hz, 2H), 2.94–2.98 (m, 4H), 3.08–3.15 (m, 2H), 4.14–4.19 (m, 6H), 4.83 (q, $^3J$ (H,H) = 6.8 Hz, 1H), 6.12 (s, 2H), 6.23 (d, $^3J$ (H,H) = 8.8 Hz, 2H), 7.22 (d, $^3J$ (H,H) = 8.8 Hz, 4H), 7.24 (d, $^3J$ (H,H) = 8.8 Hz, 2H), 7.58 (d, $^3J$ (H,H) = 8.0 Hz, 2H), 7.63 (d, $^3J$ (H,H) = 8.8 Hz, 2H), 8.04 (s, 1H), 8.12 (d, $^3J$ (H,H) = 8.8 Hz, 4H), 8.15 (d, $^3J$ (H,H) = 8.0 Hz, 4H), 8.95 (d, $^3J$ (H,H) = 4.8 Hz, 2H; β-H), 9.01 (d, $^3J$ (H,H) = 4.8 Hz, 2H; β-H), 9.02 ppm (s, 4H; β-H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta=14.6$, 17.8, 23.1, 26.6, 29.6, 29.8, 32.2, 45.4, 46.7, 50.5, 52.2, 68.3, 70.0, 110.6, 112.2, 114.0, 117.6, 119.6, 120.5, 120.6, 130.9, 131.2, 131.5, 134.4, 134.7, 135.0, 135.2, 135.8, 149.5, 149.9, 150.0, 150.1, 158.0, 164.7, 168.2 ppm; IR (KBr): $\tilde{\nu}=3417$, 3329, 3031, 2925, 2851, 1704, 1679, 1603, 1524, 1508, 1489, 1467, 1381, 1338, 1270, 1239, 1169, 1090, 995, 796, 720 cm$^{-1}$; HRMS (FAB): *m/z*: calcd for 1384.6683 ($C_{87}H_{96}N_6O_6$, [$M^+$]); found: 1384.6677.

**Compound 1i**: In a manner similar to that described for **1c**, **1j** (66 mg, 0.05 mmol) was transformed into **1i** as a purple solid (67 mg, 97%): m.p.: 119–120°C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta=1.02$ (t, $^3J$ (H,H) = 6.8 Hz, 9H), 1.37–1.65 (m, 32H), 1.84 (d, $^3J$ (H,H) = 6.8 Hz, 3H), 1.91–1.99 (m, 6H), 2.85 (d, $^3J$ (H,H) = 11.2 Hz, 2H), 2.96 (br, 4H), 3.07–3.10 (m, 2H), 4.13–4.18 (m, 6H), 5.14 (q, $^3J$ (H,H) = 6.8 Hz, 1H), 6.15 (s, 2H), 6.22 (d, $^3J$ (H,H) = 8.8 Hz, 2H), 7.20–7.25 (m, 6H), 7.46 (d, $^3J$ (H,H) = 8.4 Hz, 2H), 7.68 (d, $^3J$ (H,H) = 8.8 Hz, 2H), 8.15 (d, $^3J$ (H,H) = 8.4 Hz, 6H), 8.26 (d, $^3J$ (H,H) = 8.0 Hz, 2H), 9.00 (d, $^3J$ (H,H) = 4.8 Hz, 2H; β-H), 9.04–9.05 ppm (m, 6H; β-H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta=14.6$, 17.5, 23.1, 26.6, 29.65, 29.78, 29.80, 30.0, 32.2, 45.4, 46.7, 50.5, 52.2, 68.3, 68.5, 110.5, 112.3, 114.4, 119.1, 119.2, 120.3, 120.5, 120.7, 131.0, 131.2, 131.5, 131.7, 134.6, 134.7, 135.0, 135.3, 140.2, 149.5, 149.91, 149.94, 150.04, 158.0, 165.6, 169.4 ppm; IR (KBr): $\tilde{\nu}=3063$, 3034, 2955, 2923, 2850, 1780, 1704, 1606, 1527, 1508, 1492, 1470, 1378, 1337, 1280, 1248, 1175, 1106, 998, 796, 770, 720 cm$^{-1}$; HRMS (FAB): *m/z*: calcd for 1385.6523 ($C_{87}H_{95}N_5O_7Zn$, [$M^+$]); found: 1385.6531.

**Polymer 2d**: A solution of **1d** (79 mg, 0.06 mmol) and [($Cy_3P$)$_2Cl_2$Ru=CHPh] (4.8 mg, 0.006 mmol) in $CH_2Cl_2$ (2 mL) was stirred under argon at room temperature for 2 h. The mixture was quenched with ethyl vinyl ether (0.2 mL) and then poured into MeOH (10 mL). The solid was collected, redissolved in $CH_2Cl_2$ (1 mL), and reprecipitated by adding MeOH (10 mL). This procedure was repeated twice, and the solid was collected to afford **2d** as a dark purple solid (79 mg, 99%): $^1$H NMR (300 MHz, $CDCl_3$): $\delta=-2.85$ (2H), 0.90 (s, 9H), 1.29–1.96 (m, 41H), 2.20–3.60 (m, 12H), 4.22 (s, 2H), 5.00–5.70 (m, 3H), 5.70–7.00 (m, 7H), 7.25 (s, 2H), 7.50–9.00 (m, 20H; phenyl and β-H), 10.01 ppm (br, 1H; CON*H*); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta=14.1$, 17.6, 22.7, 26.1, 29.3, 29.4, 31.8, 43–45 (br), 49–51 (br), 67.3, 68.2, 110–113 (br, embodied a sharp peak at 112.6), 117–120 (br), 127–136 (br, embodied three sharp peaks at 133.1, 134.4 and 135.5), 157.8, 158.9 ppm; IR (KBr): $\tilde{\nu}=3313$, 2926, 2854, 1691, 1606, 1509, 1470, 1401, 1377, 1351, 1285, 1245, 1174, 1108, 966, 801, 735 cm$^{-1}$; GPC (THF): $M_n=14820$; $M_w=16470$; PDI = 1.11.

**2f:** (93%): GPC (THF): $M_n=11460$; $M_w=12660$; PDI = 1.11.

**2c:** (96%): $^1$H NMR (300 MHz, $CDCl_3$): $\delta=0.93$ (s, 9H), 1.30–1.96 (m, 41H), 2.20–3.60 (m, 8H), 4.22 (br, 6H), 5.00–6.00 (m, 3H), 6.00–7.26 (m, 9H), 7.27–7.50 (br, 2H), 7.60–8.40 (m, 10H), 8.40–9.50 ppm (m, 9H; β-H and CON*H*); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta=14.2$, 22.7, 26.2, 29.4, 29.5, 31.9, 35.3, 42–52 (v br), 67–69 (br), 110–114 (br), 119–121 (br), 128.6, 130–133 (br), 133–136 (br), 149–151 (br), 157–159 ppm (br); IR (KBr): $\tilde{\nu}=2925$, 2854, 1698, 1606, 1525, 1509, 1492, 1473, 1377, 1339, 1245, 1174, 1108, 1068, 998, 798, 719 cm$^{-1}$; GPC (THF): $M_n=14190$; $M_w=16080$; PDI = 1.13.

**2e**: (95%): GPC (THF): $M_n=13670$; $M_w=15440$; PDI = 1.13.

**2h**: (98%): $^1$H NMR (400 MHz, $CDCl_3$): $\delta=-2.76$ (s, 2H), 0.88 (br, 9H), 1.28–1.90 (m, 41H), 2.37 (br, 4H), 2.91 (br, 4H), 3.81 (br, 4H), 4.11 (br, 2H), 5.09 (br, 2H), 5.58 (br, 1H), 6.30 (br, 2H), 6.87 (br, 4H), 7.15 (br, 2H), 7.50–8.20 (m, 12H), 8.50–8.80 ppm (m, 9H; NH and β-H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta=14.1$, 17.8, 22.7, 26.1, 26.9, 29.3, 31.8, 35.6, 36.9, 44.2, 46.1, 49.2, 68.2, 70.8, 111.5, 112.6, 115.7, 118.2, 119.0, 119.8, 131.6, 134.1, 134.9, 135.4, 137.0, 138.4, 151.1, 158.9, 165.9, 169.4 ppm; IR (KBr): $\tilde{\nu}=3420$, 3316, 3028, 2920, 2847, 1704, 1606, 1525, 1507, 1470, 1375, 1347, 1277, 1239, 1169, 1096, 1030, 966, 799, 732 cm$^{-1}$; GPC (THF): $M_n=17600$; $M_w=19300$; PDI = 1.09.

**2g**: (90%): $^1$H NMR (400 MHz, $CDCl_3$): $\delta=0.88$ (br, 9H), 1.28–1.90 (m, 41H), 2.49 (br, 4H), 2.87 (br, 4H), 3.91 (br, 7H), 5.07 (br, 2H), 6.11 (br, 2H), 7.04 (br, 6H), 7.26–7.50 (m, 4H), 7.94 (br, 9H), 8.70–9.00 ppm (m, 8H; β-H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta=14.1$, 17.1, 22.7, 26.1, 29.4, 31.8, 35.3, 37.0, 44.2, 46.1, 49.2, 68.1, 69.9, 111.3, 112.5, 115.2, 117.7, 119.8, 120.7, 131.9, 134.8, 135.4, 139.3, 150.0, 150.5, 158.6, 165.3, 168.5 ppm; IR (KBr): $\tilde{\nu}=3411$, 3031, 2925, 2853, 1708, 1603, 1525, 1507, 1377, 1337, 1264, 1239, 1175, 1093, 995, 799, 717 cm$^{-1}$; GPC (THF): $M_n=15500$; $M_w=17400$; PDI = 1.12.

**2j**: (95%): $^1$H NMR (400 MHz, $CDCl_3$): $\delta=-2.76$ (s, 2H), 0.91 (br, 9H), 1.28–1.90 (m, 41H), 2.56 (br, 4H), 3.11 (br, 4H), 3.94–4.20 (m, 6H), 5.16 (br, 2H), 5.52 (br, 1H), 6.41 (br, 2H), 7.02–7.26 (m, 6H), 7.41 (br, 2H), 7.80–8.00 (m, 10H), 8.68 ppm (br, 8H; β-H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta=14.3$, 17.3, 22.8, 26.3, 29.4, 29.5, 29.6, 29.8, 32.0, 35.8, 36.2, 44.4, 46.4, 49.3, 68.1, 68.8, 111.3, 112.5, 115.8, 118.3, 119.5, 119.8, 120.0, 131.0, 131.6, 134.0, 135.1, 135.3, 139.8, 150.1, 150.9, 158.7, 166.1, 169.9 ppm; IR (KBr): $\tilde{\nu}=3313$, 3028, 2930, 2851, 1770, 1708, 1603, 1511, 1473, 1372, 1343, 1274, 1242, 1176, 1100, 967, 802, 736 cm$^{-1}$; GPC (THF): $M_n=16490$; $M_w=19630$; PDI = 1.19.

  

**2i**: (87%): $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.92 (br, 9H), 1.33–1.83 (m, 41H), 2.63 (br, 4H), 3.02 (br, 4H), 4.08 (br, 6H), 5.20 (br, 3H), 6.28 (br, 2H), 7.14 (br, 6H), 7.34 (br, 2H), 7.69 (br, 2H), 8.03 (br, 8H), 8.91 ppm (br, 8H; β-H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 14.1, 17.1, 22.7, 26.2, 29.3, 29.4, 29.7, 31.8, 44.4, 46.3, 49.4, 68.2, 68.6, 111.3, 112.5, 115.7, 119.4, 120.8, 121.0, 125.9, 128.5, 131.6, 131.9, 132.0, 135.0, 135.4, 140.6, 145.2, 149.9, 150.4, 150.7, 151.0, 158.7, 166.2, 170.0 ppm; IR (KBr): $\tilde{\nu}$ = 3037, 2955, 2923, 2854, 1771, 1711, 1606, 1520, 1505, 1489, 1470, 1375, 1340, 1271, 1245, 1175, 1100, 998, 799, 770, 723 cm$^{-1}$; GPC (THF): $M_n$ = 12760; $M_w$ = 14500; PDI = 1.14.

**2b** (94%): $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = −2.77 (s, 2H), 0.83 (br, 9H), 1.22–1.98 (m, 38H), 2.00–3.50 (br, 8H), 3.72–4.25 (br, 6H), 5.24 (br, 2H), 6.51–7.26 (m, 8H), 7.58 (br, 2H), 7.77 (br, 4H), 8.00–8.20 (m, 6H), 8.71–8.81 ppm (m, 8H; β-H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 14.1, 22.7, 26.1, 26.2, 29.2, 29.3, 29.5, 29.7, 30.2, 31.8, 39.8, 44.4, 46.7, 47.5, 49.2, 67.9, 68.3, 111.6, 112.4, 112.7, 116.2, 118.8, 119.9, 120.2, 126.1, 128.6, 131.0, 132.2, 134.0, 135.3, 135.9, 139.4, 151.2, 158.7, 158.9, 165.6 ppm; IR (KBr): $\tilde{\nu}$ = 3315, 2924, 2853, 1726, 1606, 1559, 1507, 1469, 1378, 1351, 1311, 1265, 1245, 1205, 1175, 1165, 1059, 966, 800, 760, 734 cm$^{-1}$; GPC (THF): $M_n$ = 28367; $M_w$ = 39764; PDI = 1.40.

**2l**: (92%): $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = −2.84 (br, 2H; NH), 0.7–0.9 (br, 9H; $CH_3$), 0.9–1.4 (m, 44H; $CH_2$), 1.4–1.9 (m, 12H; $CH_2$), 2.1–2.8 (m, 8H), 2.8–3.3 (m, 4H), 4.5–4.8 (m, 6H), 5.0–5.1 (m, 2 H), 5.6 (br, 2H), 6.4 (br, 2H),7.6 (br, 2H), 7.9 (br, 2H), 8.1 (br, 2H), 8.6 (br, 2H), 9.0–9.4 ppm (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 14.1, 22.6, 29.28, 29.34, 29.6, 29.7, 30.4, 30.6, 31.9, 35.2, 38.5, 38.9, 44.8, 49.2, 65.8, 111.4, 118.9, 125.9, 131.6, 134.4, 136.1, 142.1, 166.9 ppm; IR (KBr): $\tilde{\nu}$ = 3316, 3126, 2955, 2923, 2852, 1705, 1606, 1522, 1479, 1373, 1270, 1177, 1096, 966, 791, 767, 733 cm$^{-1}$; GPC (THF): $M_n$ = 11000; $M_w$ = 12000; PDI = 1.13.

**Copolymer 3**: A solution of **1a** (40 mg, 0.030 mmol), **1b** (26 mg, 0.020 mmol) and [$(Cy_3P)_2Cl_2Ru$=CHPh] (4 mg, 0.005 mmol) in $CH_2Cl_2$ (2 mL) was stirred under argon at room temperature for 2 h. The reaction was quenched with ethyl vinyl ether (0.5 mL), and the solution was added dropwise into MeOH (10 mL). The solid was collected and redissolved in $CH_2Cl_2$ (1 mL) and reprecipitated by adding MeOH (10 mL). This procedure was repeated twice, and the solid was collected to afford **3** as a purple solid (55 mg, 85%): $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = −2.78 (s, 0.79H; NH), 0.84 (br, 9H), 1.25–1.90 (m, 38H), 2.20–3.50 (br, 8H), 3.74 (br, 4H), 4.15 (br, 2H), 5.22 (br, 2H), 6.41 (br, 2H), 6.83 (br, 4H), 7.19 (br, 2H), 7.53 (br, 2H), 7.80–8.19 (m, 10H), 8.41–8.90 ppm (m, 8H; β-H); IR (KBr): $\tilde{\nu}$ = 2925, 2854, 1725, 1605, 1525, 1508, 1469, 1379, 1339, 1272, 1245, 1205, 1175, 1165, 1061, 998, 966, 799, 720 cm$^{-1}$; GPC (THF): $M_n$ = 14390; $M_w$ = 16200; PDI = 1.12.

**4**: (93%): $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = −2.81 (s, 2H; NH), 0.93 (br, 18H), 1.34–1.99 (m, 82H), 2.20–3.60 (m, 24H), 4.25 (br, 4H), 5.31 (br, 6H), 6.40–7.26 (m, 18H), 7.26–8.30 (m, 25H), 8.56–8.90 (m, 8H; β-H), 9.79 ppm (br, 1H); IR (KBr): $\tilde{\nu}$ = 3310, 3034, 2927, 2851, 1695, 1679, 1605, 1527, 1508, 1467, 1379, 1331, 1280, 1239, 1175, 1106, 1061, 995, 966, 802, 723 cm$^{-1}$; GPC (THF): $M_n$ = 13400; $M_w$ = 14900; PDI = 1.11.

**5**: (98%): $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = −2.77 (s, 2H; NH), 0.87 (br, 18H), 1.27–1.99 (m, 82H), 2.20–3.60 (m, 16H), 3.86–4.10 (br, 12H), 5.06 (br, 6H), 6.19 (br, 4H), 6.94–7.26 (m, 12H), 7.51–8.10 (m, 26H), 8.80–8.86 ppm (m, 16H; β-H); IR (KBr): $\tilde{\nu}$ = 3414, 3316, 3034, 2927, 2847, 1704, 1605, 1525, 1511, 1470, 1381, 1339, 1274, 1245, 1205, 1175, 1099, 998, 963, 799, 726 cm$^{-1}$; GPC (THF): $M_n$ = 18000; $M_w$ = 20300; PDI = 1.12.

**6**: (93%): $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = −2.77 (s, 2H; NH), 0.90 (br, 18H), 1.28–2.00 (m, 82H), 2.40–3.40 (m, 16H), 3.97–4.08 (br, 12H), 5.18 (br, 6H), 6.33 (br, 4H), 7.04–7.26 (m, 12H), 7.37 (br, 4H), 7.60–8.20 (m, 20H), 8.79–8.88 ppm (m, 16H; β-H); IR (KBr): $\tilde{\nu}$ = 3310, 3028, 2925, 2854, 1774, 1709, 1605, 1523, 1506, 1469, 1379, 1339, 1272, 1245, 1205, 1175, 1102, 997, 966, 799, 767, 732 cm$^{-1}$; GPC (THF): $M_n$ = 17500; $M_w$ = 19500; PDI = 1.11.

**Copolymer 7**: A solution of **k** (57 mg, 0.05 mmol), **l** (60 mg, 0.05 mmol) and [$(Cy_3P)_2Cl_2Ru$=CHPh] (4 mg, 0.005 mmol, 10 mol%) in $CH_2Cl_2$ (5 mL) was stirred under argon at room temperature for 2 h. The reaction was quenched with ethyl vinyl ether (1.0 mL) and the solution was added dropwise into MeOH (20 mL). The solid was collected and redissolved in $CH_2Cl_2$ (2 mL) and reprecipitated by adding MeOH (10 mL). This procedure was repeated twice, and the solid was collected to afford **7** as a purple solid (108 mg, 92%): $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = −2.97 (br, 2H), 0.7–0.9 (br, 18H), 0.9–1.7 (br, 88H), 1.7–2.2 (br, 14H), 2.1–2.8 (br, 18H), 2.8–3.4 (br, 8H), 4.0–4.9 (br, 10H), 4.9–5.4 (br, 4H), 5.4–5.8 (br, 4H), 6.2–6.8 (br, 4H), 7.5–7.8 (br, 4H), 7.8–8.2 (br, 8H), 8.5–9.5 ppm (br, 14H); IR (KBr): $\tilde{\nu}$ = 3313, 3120, 3028, 2949, 2923, 2851, 1705, 1605, 1522, 1479, 1466, 1375, 1271, 1178, 1097, 967, 790, 767 cm$^{-1}$; GPC (THF): $M_n$ = 11600; $M_w$ = 14400; PDI = 1.24.

**2-(4-Bromophenyl)-4-β-styryl-6-vinyloctahydrocyclopenta[*c*]pyrrole (19)**: A solution of **18** (10.0 g, 31.43 mmol), styrene (9.0 mL, 78.6 mmol), and Grubbs I catalyst (1.29 g, 1.57 mmol) in $CH_2Cl_2$ (150 mL) was stirred under argon for 24 h and quenched with ethyl vinyl ether (10 mL). Removal of the solvent in vacuo, followed by chromatographic purification (silica gel, hexane/$CH_2Cl_2$ = 1:1) afforded **19** (9.96 g, 75%): m.p.: 131–132 °C; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 1.56–1.66 (m, 1H), 2.08–2.14 (m, 1H); 3.04–3.20 (m, 2H), 3.39–3.47 (m, 2H), 5.17–5.22 (m, 2H), 6.05–6.13 (m, 1H), 6.45–6.54 (m, 2H), 7.16 (d, $^3J$ (H,H) = 8.7 Hz, 2H), 7.20–7.41 (m, 5H), 7.58 ppm (d, $^3J$ (H,H) = 8.7 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 35.9, 45.7, 46.2, 48.7, 49.4, 116.0, 122.2, 126.3, 127.4, 127.8, 127.9, 128.5, 130.8, 131.0, 132.2, 136.0, 137.0, 175.2, 175.3 ppm; IR (KBr): $\tilde{\nu}$ = 3085, 3056, 3025, 2956, 2923, 2854, 1776, 1712, 1490, 1449, 1377, 1178, 1071, 1013, 964, 924, 804, 749, 695 cm$^{-1}$; HRMS (FAB): *m/z*: calcd for: 422.0756 ($C_{23}H_{21}NO_2Br$, , [$M^+$+H]); found: 422.0759.

To a slurry of $LiAlH_4$ (7.2 g, 189 mmol) in $Et_2O$ (100 mL) was added slowly **19** (10.0 g, 23.68 mmol) in $CH_2Cl_2$ (100 mL), and the mixture was stirred at room temperature for 1 h. Ethyl acetate was carefully added, water (1 mL) was then introduced, and the resulting suspension was filtered, and the organic layer was evaporated in vacuo to give a residue, which was triturated with $CH_2Cl_2$ repeatedly. The $CH_2Cl_2$ solution was dried ($MgSO_4$) and filtered. The solvent was removed in vacuo to give **20** as a colorless liquid (7.84 g, 84%): $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.64 (q, $^2J$ (H,H) = 12.0 Hz, 1H), 1.96 (dt, $^2J$ (H,H) = 12.4; $^3J$ (H,H) = 6.0 Hz, 1H), 2.80–2.86 (m, 1H), 2.91–3.04 (m, 3H), 3.15–3.21 (m, 4H), 5.08 (dd, $^3J$ (H,H) = 9.4 Hz, $^2J$ (H,H) = 1.6 Hz, 1H), 5.09 (dd, $^3J$ (H,H) = 17.2 Hz, $^2J$ (H,H) = 1.6 Hz, 1H), 5.85 (ddd, $^3J$ (H,H) = 17.2 Hz, $^3J$ (H,H) = 9.4 Hz, $^3J$ (H,H) = 7.2 Hz, 1H), 6.20 (dd, $^3J$ (H,H) = 16.0 Hz, $^3J$ (H,H) = 7.6 Hz, 1H), 6.43 (d, $^3J$ (H,H) = 16.0 Hz, 1H), 6.69 (d, $^3J$ (H,H) = 8.8 Hz, 1H), 7.19–7.34 ppm (m, 7H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 35.2, 45.3, 46.0, 46.2, 46.7, 50.2, 50.3, 108.5, 114.8, 115.4, 126.0, 127.1, 128.5, 130.6, 130.9, 131.6, 137.4, 138.9, 147.4 ppm; IR (KBr): $\tilde{\nu}$ = 3078, 3024, 2943, 2834, 1638, 1593, 1494, 1479, 1366, 1184, 1075, 996, 964, 913, 807, 747, 693 cm$^{-1}$; HRMS (FAB): *m/z*: calcd for 393.1092 ($C_{23}H_{24}NBr$, [$M^+$+H]); found: 393.1098.

**4-(4-Styryl-6-vinylhexahydro-cyclopenta[*c*]pyrrol-2-yl)benzoic acid methyl ester (22)**: To a solution of **20** (9.24 g, 23.43 mmol) in THF (250 mL) cooled to −78 °C was added dropwise *n*BuLi (11.3 mL, 2.5 M in hexane, 28.1 mmol) under argon. The reaction mixture was stirred at −78 °C for 1 h, and then excess $CO_2$ gas was bubbled into the solution until white solid was precipitated. The mixture was gradually warmed to room temperature, poured into a mixture of $Et_2O$ (200 mL) and $H_2O$ (200 mL), and filtered, and then the filter cake was washed with $Et_2O$ (2×100 mL). The combined filtrates were acidified with 10% HCl (until pH 6). The solid was filtered and washed with $Et_2O$ (2×50 mL) to give **21** as a white solid (5.98 g, 71%): m.p.: 198–199 °C; $^1$H NMR (400 MHz, DMSO): $\delta$ = 1.60 (q, $^2J$ (H,H) = 12.6 Hz, 1H), 1.99 (dt, $^2J$ (H,H) = 12.6 Hz; $^3J$ (H,H) = 6.3 Hz, 1H), 2.80–2.87 (m, 1H), 2.91–3.03 (m, 3H), 3.17–3.24 (m, 2H), 3.27–3.34 (m, 2H), 5.04 (d, $^3J$ (H,H) = 10.3 Hz, 1H), 5.08 (d, $^3J$ (H,H) = 17.3 Hz, 1H), 5.81 (ddd, $^3J$ (H,H) = 7.2 Hz; $^3J$ (H,H) = 10.3 Hz; $^3J$ (H,H) = 17.3 Hz, 1H), 6.27 (dd, $^3J$ (H,H) = 7.2 Hz, 15.9 Hz, 1H), 6.44 (d, $^3J$ (H,H) = 15.9 Hz, 1H), 6.58 (d, $^3J$ (H,H) = 8.7 Hz, 2H), 7.18 (t, $^3J$ (H,H) = 6.5 Hz, 1H), 7.25–7.29 (m, 2H), 7.36 (d, $^3J$ (H,H) = 8.0 Hz, 2H), 7.72 (d, $^3J$ (H,H) = 8.7 Hz, 2H), 12.06 ppm (brs, 1H); $^{13}$C NMR (100 MHz, DMSO): $\delta$ = 34.7, 44.5, 45.1, 45.6, 46.2, 49.3, 49.4, 111.7, 115.4, 119.0, 125.9, 127.0, 128.5, 130.0, 130.8, 131.2, 137.1, 139.3, 150.5, 168.1 ppm; IR (KBr): $\tilde{\nu}$ = 3430, 3069, 3028, 2930, 2857, 2664, 2537, 1654,

  

1599, 1525, 1417, 1383, 1289, 1181, 1124, 963, 919, 774 $cm^{-1}$; HRMS (FAB): $m/z$: calcd for 360.1964 ($C_{24}H_{26}NO_2$, [$M^+$+H]); found: 360.1962.

To a solution of **21** (3.0 g, 8.3 mmol) in $CH_2Cl_2$ (30 mL) at 0 °C was added oxalyl chloride (0.9 mL, 10.5 mmol) and DMF (one drop). The mixture was gradually warmed to room temperature and stirred for 1 h. The solvent was removed in vacuo to give the crude acid chloride, which was used for the next reaction without further purification. To a mixture of dry methanol (20 mL) and dry THF (30 mL) was added acid chloride in THF (10 mL) at 0 °C. The mixture was stirred at room temperature for 8 h. Saturated $NaHCO_3$ was added and the solution was washed with water and brine and then dried ($MgSO_4$). The solvent was removed in vacuo, and the residue was chromatographed on silica gel (hexane/$CH_2Cl_2$ = 2:1) to give **22** as light yellowish liquid (2.87 g, 92 %): $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.62 (q, $^2J$ (H,H) = 12.0 Hz, 1H), 1.97 (dt, $^2J$ (H,H) = 12.0 Hz, $^3J$ (H,H) = 6 Hz; 1H), 2.80–2.87 (m, 1H), 2.92–3.02 (m, 3H), 3.26–3.35 (m, 4H), 3.84 (s, 3H), 5.05–5.11 (m, 2H), 5.81 (ddd, $^3J$ (H,H) = 17.2 Hz; $^3J$ (H,H) = 10.4 Hz; $^3J$ (H,H) = 7.2 Hz, 1H), 6.15 (dd, $^3J$ (H,H) = 15.6 Hz; $^3J$ (H,H) = 7.6 Hz, 1H), 6.42 (d, $^3J$ (H,H) = 15.6 Hz, 1H), 6.54 (d, $^3J$ (H,H) = 9.0 Hz, 2H), 7.16–7.22 (m, 1H), 7.26–7.32 (m, 4H), 7.87 ppm (d, $^3J$ (H,H) = 9.0 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 35.2, 45.1, 45.8, 46.2, 46.7, 49.5, 49.6, 51.4, 111.5, 115.5, 116.9, 125.8, 127.0, 128.3, 130.5, 130.6, 131.0, 137.0, 138.6, 150.7, 167.2 ppm; IR (KBr): $\tilde{\nu}$ = 3075, 3053, 3024, 2945, 2917, 2850, 1705, 1606, 1522, 1480, 1434, 1379, 1280, 1180, 1107, 970, 914 $cm^{-1}$; HRMS (FAB): $m/z$: calcd for 374.2120 ($C_{25}H_{28}NO_2$, [$M^+$+H]); found: 374.2119.

**Dimer 23**: A solution of **22** (1.62 g, 4.33 mmol) and Grubbs II catalyst **24** (187 mg, 0.22 mmol) in $CH_2Cl_2$ (40 mL) was heated at reflux under nitrogen for 24 h, cooled to room temperature, and quenched with ethyl vinyl ether (5 mL). Removal of the solvent in vacuo, followed by chromatographic purification (silica gel, hexane/$CH_2Cl_2$ = 1:2) afforded **23** (870 mg, 28 %): m.p.: 190–191 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.53–1.63 (m, 2H), 1.92–1.97 (m, 2H), 2.80–2.85 (m, 2H), 2.94–3.02 (m, 6H), 3.19–3.37 (m, 8H), 3.84 (s, 3H), 3.85 (s, 3H), 5.44–5.49 (m, 2H), 6.16 (dd, $^3J$ (H,H) = 7.0 Hz; $^3J$ (H,H) = 14.2 Hz, 1H), 6.20 (dd, $^3J$ (H,H) = 7.2 Hz; $^3J$ (H,H) = 14.2 Hz, 1H), 6.41 (d, $^3J$ (H,H) = 14.2 Hz, 1H), 6.42 (d, $^3J$ (H,H) = 14.2 Hz, 1H), 6.51 (d, $^3J$ (H,H) = 9.0 Hz, 2H), 6.56 (d, $^3J$ (H,H) = 9.0 Hz, 2H), 7.20–7.25 (m, 2H), 7.26–7.33 (m, 8H), 7.88 (d, $^3J$ (H,H) = 9.0 Hz, 2H), 7.90 ppm (d, $^3J$ (H,H) = 9.0 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 35.7, 35.9, 44.6, 44.8, 45.1, 45.2, 46.2, 46.5, 46.8, 46.9, 49.4, 49.55, 49.59, 51.4, 111.40, 111.43, 116.9, 117.0, 125.8, 127.0, 128.32, 128.34, 130.3, 130.4, 130.6, 131.1, 131.56, 131.62, 137.0, 150.6, 150.7, 167.1 ppm; IR (KBr): $\tilde{\nu}$ = 3053, 3025, 2945, 2917, 2851, 1702, 1605, 1522, 1479, 1434, 1380, 1280, 1180, 1107, 970 $cm^{-1}$; HRMS (FAB): $m/z$: calcd for 718.3771 ($C_{48}H_{50}N_2O_4$, [$M^+$+H]); found: 718.3768.

**Dimer 16**: To a solution of **23** (450 mg, 0.62 mmol) in THF (20 mL) and MeOH (5 mL) at 0 °C was added NaOH (55 mg, 1.37 mmol). The mixture was heated at reflux for 4 h and cooled to room temperature. After most of the solvent was removed, $Et_2O$ (20 mL) and $H_2O$ (30 mL) was added, and the aqueous layer was acidified with 10 % HCl (until pH 6). The solid was filtered to give the diacid as a white solid, which was used for the next reaction without further purification.

To a solution of diacid (60 mg, 0.09 mmol) in $CH_2Cl_2$ (10 mL) at 0 °C was added oxalyl chloride (0.2 mL) and DMF (one drop). The mixture was gradually warmed to room temperature and stirred for 1 h. The solvent was removed in vacuo to give crude acid chloride, which was taken up in $CH_2Cl_2$ (10 mL) and added to a cooled (0 °C) solution of **11L** (200 mg, 0.18 mmol), $NEt_3$ (0.5 mL), and a trace amount of DMAP in $CH_2Cl_2$ (10 mL). The mixture was stirred at room temperature for 17 h. Saturated $NaHCO_3$ was added and the solution was washed with water and brine and then dried ($MgSO_4$). The solvent was removed in vacuo, and the residue was chromatographed on silica gel (hexane/$CH_2Cl_2$/$NEt_3$ = 1:2:0.05) to give **16** (183 mg, 72 %): m.p.: 179–180 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = −2.80 (s, 4H), 0.86–1.22 (m, 18H), 1.25–1.80 (m, 70H), 1.81–2.12 (m, 12H), 2.78–3.59 (m, 24H), 4.29 (m, 4H), 5.41–5.47 (m, 2H), 5.64–5.78 (m, 2H), 5.94–6.00 (m, 4H), 6.14–6.26 (m, 2H), 6.40–6.50 (m, 2H), 6.57–6.65 (m, 4H), 6.72–6.77 (m, 2H), 7.05–7.38 (m, 18H), 7.74–8.78 (m, 40H), 9.85–9.95 ppm (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 14.3, 22.9, 26.3, 26.4, 29.5, 29.6, 32.0, 44.2, 45.0, 45.1, 45.9, 46.1, 46.4, 49.8, 50.1, 65.2, 67.4, 67.5, 68.3, 111.5, 112.1, 112.6, 118.6, 118.9, 119.1, 119.2, 119.3, 119.6, 120.1, 120.7, 125.80, 125.87, 125.91, 126.8, 127.1, 127.4, 128.33, 128.36, 128.40, 129.3, 129.7, 130.3, 130.6, 130.7, 131.1, 133.2, 133.3, 134.3, 134.9, 135.4, 137.0, 137.1, 137.7, 138.2, 150.3, 150.4, 150.5, 157.8, 157.9, 158.7, 168.4, 172.2, 172.4 ppm; IR (KBr): $\tilde{\nu}$ = 3316, 3113, 3056, 3025, 2926, 2854, 1679, 1606, 1508, 1470, 1376, 1350, 1284, 1245, 1174, 1108, 966 $cm^{-1}$; HRMS (MALDI): $m/z$: calcd for 2826.8442 ($C_{188}H_{211}N_{14}O_{10}$, [$M^+$+H]); found: 2826.8452.

**Dimer 17**: A mixture of **16** (110 mg, 0.039 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (180 mg, 0.80 mmol) in methanol (10 mL) and $CH_2Cl_2$ (20 mL) was stirred at room temperature in the dark for 3 h and then washed with $NaHCO_3$ and brine, and dried ($MgSO_4$). The solvent was removed in vacuo to give a residue, which was chromatographed on silica gel (hexane/$CH_2Cl_2$/$NEt_3$ = 1:2:0.05) to afford **17** (102 mg, 89 %): m.p.: 215–216 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.92–0.96 (m, 18H), 1.17–2.05 (m, 82H), 2.84–3.52 (m, 24H), 4.17–4.25 (m, 4H), 5.50–5.64 (m, 2H), 6.03–6.59 (m, 16H), 6.85–7.37 (m, 18H), 7.88–8.35 (m, 20H), 8.52–8.92 ppm (m, 18H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 14.3, 22.9, 26.3, 29.46, 29.52, 29.58, 29.63, 29.8, 32.0, 44.4, 45.2, 46.3, 46.7, 49.8, 67.7, 68.2, 111.6, 112.4, 118.2, 118.6, 119.8, 120.3, 120.5, 125.8, 125.9, 127.1, 128.3, 128.4, 130.3, 130.7, 131.5, 134.3, 134.6, 135.1, 135.3, 137.0, 139.0, 149.7, 149.9, 150.0, 157.8, 158.4, 166.8, 167.3, 171.0 ppm; IR (KBr): $\tilde{\nu}$ = 3037, 2955, 2918, 2850, 1733, 1605, 1524, 1508, 1467, 1244, 1174, 996, $cm^{-1}$; HRMS (MALDI): $m/z$: calcd for 2953.6050 ($C_{188}H_{207}N_{14}O_{10}{}^{65}Zn_2$, [$M^+$+H]); found: 2953.6060.

**Time-resolved fluorescence experiments**: A mode-locked Ti:sapphire laser (wavelength: 850 nm; repetition rate: 76 MHz; pulse width: < 200 fs) was passed through an optical parametric amplifier to produce 425 nm pulse laser. The fluorescence of sample was reflected by a grating (150 g $mm^{-1}$; BLZ: 500 nm) and detected by an optically triggered streak camera (Hamamatsu C5680) with a time resolution of about 0.3 ps. The sample was prepared with $1\times10^{-5}$ M concentration in $CH_2Cl_2$, and using ultramicrocuvette with 1 mm pathlength to maintain the excitation at the same time. The signal was collected 50 times to increase the signal to noise ratio.

**DFT calculations**: DFT calculations[30] at the GGA/BLYP/DNP level implemented with the DMol$^3$ program package were used for geometric optimization of **25**.[31] The electronic configuration of the molecular systems was described by a double-numerical plus polarization (DNP) basis set comparable to the Gaussian 6-31G** basis sets.[31] The local exchange-correlation potential[32] was augmented in a self-consistent manner with Becke exchange[33] and Lee–Yang–Parr correlation[34] gradient corrections, giving a generalized gradient approximation (GGA/BLYP) for the evaluation of energies and geometries. Convergence criteria for geometry optimizations were, generally, the threshold values: $2\times10^{-5}$ Hartree, 0.004 Hartree/Å, 0.005 Å, and $1\times10^{-5}$ Hartree for energy, force, displacement, and self-consistent field (SCF) density, respectively. In order to obtain precise results, neither direct inversion of iterative subspace (DIIS) to accelerate convergence of the SCF algorithm nor smearing techniques were used.

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