HETEROCYCLES, Vol. 57, No. 11, 2002, pp. 2107 - 2114, Received, 12th August, 2002

SYNTHESIS OF TROPOCRYPTANDS HAVING HETEROATOMS IN LINKER CHAINS: A NEW CLASS OF MACROBICYCLIC LIGANDS DERIVED BY *N*-ACYLATION AND *N*-ALKYLATION OF TROPOCORONAND

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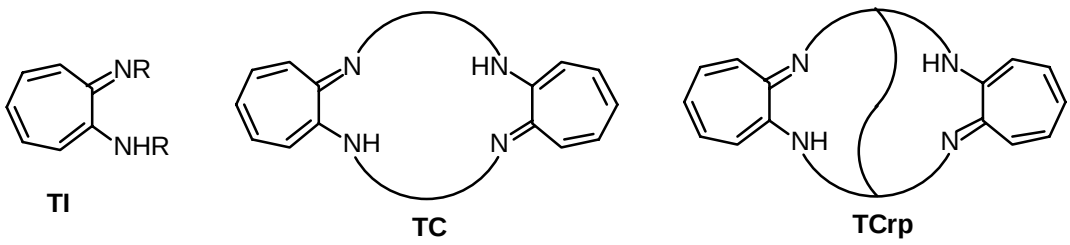
Abstract – Tropocoronand (**1**) reacted with acyl chlorides on endocyclic secondary alkylamines to afford diacyl tropocoronands (**2a** – **2c**). Double *N*-acylation of **1** with dioyl dichlorides (**3a** – **3d**) yielded amide-bridged tropocryptands (**4a** – **4d**). The similar reactions of **1** with ethylene glycol di-*p*-tosylate (**5**) or oligo(ethylene glycol) di-*p*-tosylate (**8a** – **8d**) afforded the corresponding tropocryptands (**6** or **9a** – **9d**).

Tropocoronands (TCs), metal-complexing non-benzenoid macrocycles having a two dimensional framework and containing two aminotroponeimine (TI)[1-3] units bridged by polymethylene, amine, ether or thioether chains, were reported two decades ago.[4] Those macrocyclic ligands and their metal complexes have been employed in transition metal chemistry[4a-c,5] and as models for bioactive molecules.[6] Macrobicyclic tropocryptands (TCrps) are three dimensional in structure containing an intramolecular cavity and comparison between TCs and TCrps is quantitatively or qualitatively interesting. The differences might be reflected in conformational properties, as well as in physical, structural, complexing and chemical properties. The investigation of TCrps, however, is few because of their synthetic difficulty.[7]

Here we describe a detailed synthetic study of a novel family of TCrps that contain two TI units bridged by diacyl, polymethylene and ether chains, *i. e.*,macrobicycles (**4**, **6** and **9**).



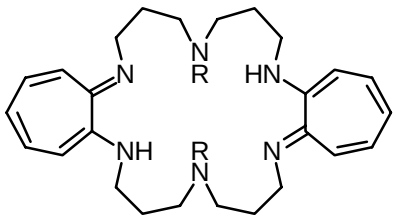
TI **TC** **TCrp**

RESULTS and DISCUSSION

Although several synthetic strategies, *i. e.*, stepwise, tripod coupling, single capping, internal template

and so on, can be considered, the best choice of ones is difficult without further specifying the chemical nature of the system under study. From careful examination of the results reported and our experience in the field of TC chemistry, we deduced that the synthesis of TCrps could be achieved by double *N*-acylation and *N*-alkylation of diazamacrocyclic TC (**1**).

First of all, we tried the reaction of **1**[4d] with acyl halides. Treatment of a solution of TC (**1**) with 5 mol *equiv.* of acetyl chloride, benzoyl chloride or pivaloyl chloride in the presence of 4-(dimethylamino)-pyridine (DMAP) in CH_2Cl_2 at room temperature afforded bis(*N*-acyl)-TC (**2a** – **2c**) as yellow needles in 83, 83 or 99 % yield, respectively (mp: 113 °C for **2a**, 209 – 210 °C for **2b**, 198 – 199 °C for **2c**). FAB-MS spectra of all synthetic TCs gave molecular ion peaks (MH^+: **2a**; *m/z* 519, **2b**; *m/z* 643, **2c**; *m/z* 603) and the IR spectra showed the absorption maxima for NH stretching vibration of TI moieties (ν_{NH}: **2a**; 3242 cm^{-1}, **2b**; 3244 cm^{-1}, **2c**; 3222 cm^{-1}, **1**; 3430 cm^{-1} for endocyclic alkylamine, 3233 cm^{-1} for TI). These spectral data indicate that the reactions occurred not on TI but on endocyclic alkylamine moieties. Compound (**2c**) showed simple ^1H NMR spectrum, while **2a** and **2b** gave complex and broad ones, respectively. These phenomena could be ascribed to a relatively large energy barrier of amide C-N bond rotation of **2a** or **2b**. Indeed we obtained their Gibbs free energy changes of 66 (for **2a**) and 63 $kJmol^{-1}$ (for **2b**) by measurement of variable temperature ^1H NMR spectra (Table 1).[8] These values compare with those of *N,N*-dimethylpropionamide. By considering the energy value of *N,N*-dimethylpivalamide, the R groups of **2c** might be free from a restricted C-N bond rotation at room temperature.



1: R = H
2a: R = COMe, 83 %
2b: R = COPh, 83 %
2c: R = CO^{t}Bu, 99%

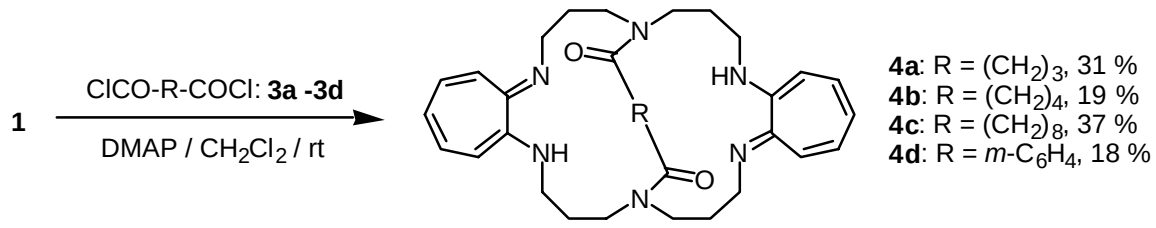
Table 1. Coalescence temperatures and energy barriers of amide C-N bond rotation of TC (**2**) and TCrp (**4**)

Substrate	**2a**	**2b**	**4a**	**4b**	**4c**	**4d**	$MeCONMe_2$	$EtCONMe_2$	$^tBuCONMe_2$
Tc [a] / K	322	309	311	321	321	314			
$\Delta G^{\ddagger}$ / $kJmol^{-1}$	66	63	67	70	67	63	80 [b]	68 [b]	47 [b]

[a] Coalescence temperature at adjacent protons of acyl groups. [b] Reference 9

Considering the results of a higher reactivity at endocyclic alkyl amines of **1**, we decided to synthesize amide-bridged TCrps by the use of double *N*-acylation of **1**. The reaction was carried out by high dilution conditions (12 $mmol \cdot l^{-1}$) to avoid oligomerization of **1** and the reagent. TC (**1**) reacted with 1.3 mol *equiv.* of glutaryl dichloride (**3a**) in the presence of DMAP (1.3 mol *equiv.*) at room temperature in CH_2Cl_2 for 23 h to afford the expected amide-bridged TCrp (**4a**) in 31 % yield. To investigate the scope and limitation of this *N*-acylation, we attempted similar reactions with some dioyl dichlrorides (Scheme 1). The reaction with adipoyl chloride (**3b**), sebacoyl chloride (**3c**) or isophthaloyl dichloride (**3d**) gave suited TCrp (**4b** – **4d**) in 19, 37 or 18 % yield, but with succinyl chloride did not proceed to the expected direction. The reason is ambiguous at this stage, but the first acylated intermediate of **1** with succinyl

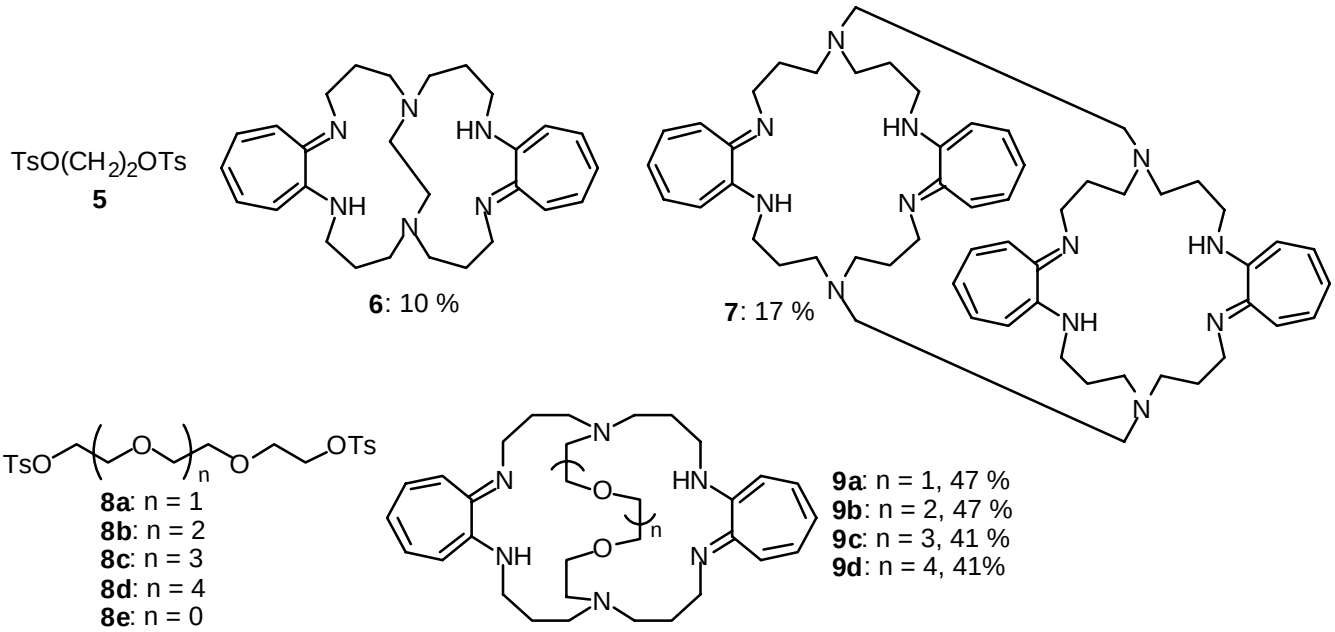
chloride might be placed in impossible conformation for ring closure, suggesting that succinyl group is the limit length as a diketo bridge chain. **4a**, **4b** and **4d** were yellow powders, while **4c** was yellow plates (mp: **4a**; 176 °C (decomp), **4b**; 234 °C (decomp), **4c**; 191 – 192 °C, **4d**; 182 – 184 °C). All synthetic TCrps showed molecular ion peaks (MH^+: **4a**; *m/z* 531, **4b**; *m/z* 545, **4c**; *m/z* 601, **4d**; *m/z* 565) in FAB-MS spectra. The NH stretching vibration of TI moieties in the IR spectra of **4** (ν_{NH}: 3224 – 3267 cm^{-1}) are almost in the same region as that of **2**. On the basis of those spectral data **4a** – **4d** were proved to be the 1 : 1 cyclization products of **1** and dioyl dichlorides, which were produced by the reaction of the latters at alkylamine moieties of the former. The complex and / or broad ^1H NMR spectra of **4** were similar to those of **2a** and / or **2b**. The Gibbs free energy changes of **4**, measured by variable temperature ^1H NMR spectral method, are listed in Table 1.[8] These values are almost equal to those of **2a** and **2b** and therefore the complexities of their ^1H NMR spectra are also ascribed to the conformers resulted by energy barriers of amide C-N bond rotation of **4**.



Scheme 1

Secondarily, we attempted the double *N*-alkylation of TC (**1**). In general, synthesis of tertialy amine by alkylation of secondary amine is quite difficult because of an easy formation of quarternary ammonium salt. However, taking into account of the steric hindrance of TCrps, the double *N*-alkylation of **1** should be possible by selecting reaction conditions. Indeed, the reaction of **1** with 1.3 mol *equiv.* of (ethylene glycol) di-*p*-tosylate (**5**) in toluene (concentration of the reaction: 12 $mmol \cdot l^{-1}$) at refluxing conditions in the presence of 5 mol *equiv.* of K_2CO_3 as a base gave expected ethylene-bridged TCrp (**6**) in 10 % yield together with its dimer (**7**) in 17 % yield. Both **6** and **7** were yellow crystals (mp: 178 – 179 °C for **6**, 187 – 190 °C for **7**) and showed molecular ion peaks in MS spectra ($M^{+\cdot}$ for EI: **6**; *m/z* 460, MH^+ for FAB: **7**; *m/z* 922). Their IR and ^1H NMR spectral and analytical data are consistent with the proposed structures. The ^1H NMR signals of adjacent protons from bridgehead nitrogen atoms of **6** were found at downfield by 0.07 and 0.28 ppm from those of **7** (δ: 2.78 *vs.* 2.71 ppm and 2.94 *vs.* 2.66 ppm) because of the strained and fixed conformation of **6** around the bridgehead moieties. To our disappointment, treatment of **1** with 1,5-dibromopentane did not form TCrp at all. In this reaction, by reason of Baldwin's rules,[10] intramolecular six-membered cyclization at one nitrogen atom might occurred and afforded a quarternary ammonium salt in preference to formation of TCrps. On the other hand, similar reactions with tri-, tetra-, penta- and hexa(ethylene glycol) di-*p*-tosylates (**8a** – **8d**) were successful. These oligo(ethylene glycol)-bridged TCrps (**9a** – **9d**) were obtained in 47, 47, 41 and 41 % yields, respectively, as yellow needles or scales (mp: **9a**; 121 – 123 °C, **9b**; 135 – 136 °C, **9c**; 93.0 – 93.5 °C, **9d**; 108 – 109 °C). In these reactions, the yields were higher than that of ethylene-bridged TCrp (**6**). The explanation for this is that template effects by potassium ion at the oligo(ethylene glycol) moieties of **8** and / or the first *N*-alkylated intermediate of **1** should be existing. The instrumental analysis data (^1H and

^{13}C NMR, IR and MS spectra and chemical analysis) of **9** are consistent with the proposed structures. In spite of the different lengths of their bridged chains, their ^{1}H NMR spectra are quite similar, indicating that oligo(ethylene glycol)-bridged TCrps (**9**) have flexible conformations differed from the strained and fixed one of ethylene-bridged TCrp (**6**). In contrast, the reaction with di(ethylene glycol) di-*p*-tosylate (**8e**) did not afford TCrp by the same reason as seen in the case of dibromopentane. Since synthetic TCrps (**9**) have two different kinds of host moieties, that is, TI moieties with high transition metal ion affinity and oligo(ethylene glycol) ones with high alkali metal ion affinity, their coordinate behaviors in the presence of a different kind of metal ions are of particular interest.



In summary, we have established the efficient synthesis of TCrps, a new family of non-benzenoid macrobicyclic ligands, by the double *N*-acylation and *N*-alkylation of TC (**1**). Further work aimed at characterizing metal coordinate properties of oligo(ethylene glycol)-bridged TCrps (**9**), which have TI and oligo(ethylene glycol) moieties, is in progress.

EXPERIMENTAL

Mps were determined with a Mitamura air-bath apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra ($SiMe_4$ as the internal standard) were determined with Bruker AC-200 and / or AC-300 spectrometers. IR spectra were determined with a Perkin Elmer System 2000 FT instrument and electronic spectra (UV-VIS) with a JASCO V-560 spectrophotometer. MS spectra were determined with JEOL JMS-DX 303 spectrometers. Unless otherwise stated the spectra were taken in the following solvents / media: IR, KBr; UV-VIS, CH_3CN; ^{1}H (200 and 300 MHz) and ^{13}C (50 and 75 MHz) NMR, $CDCl_3$; MS spectra were taken at 70 eV by electron impact (EI) and fast atom bombardment (FAB) method. The progress of most reactions was followed by TLC using Merck Aluminum oxide $60F_{254}$ neutral and / or Silica gel $60F_{254}$.

Typical experimental procedure for the synthesis of bis(*N*-acyl)-TCs (2a – 2c): To a solution of **1** (50.0 mg, 0.115 mmol) and 5 mol *equiv.* of DMAP in 10 mL of dry CH_2Cl_2, 5 mol *equiv.* of acetyl

chloride, benzoyl chloride or pivaloyl chloride was added under N_2. The reaction mixture was stirred at rt for 23 h and quenched with water. The aqueous layer was extracted with CH_2Cl_2, and the organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by aluminum oxide column chromatography (eluted by CH_2Cl_2 / EtOAc = 1 / 1) and then recrystallized from acetonitrile to give bis(*N*-acyl)-TC (**2**). **2a**: yield 83 %; yellow needles, mp 113 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.05 (8H, quint, J = 6.7 Hz), 2.13 (6H, s), 3.26 – 3.37 (8H, m), 3.53 (4H, m), 3.63 (4H, t, J = 6.7 Hz), 6.14 – 6.41 (6H, m), 6.73 – 6.85 (4H, m); IR (KBr, cm^{-1}) ν 3242, 2927, 2857, 1645, 1590, 1538, 1516; MS (FAB(+), NBA, %) *m*/*z* 519 (MH^+, 49); Anal. Calcd for $C_{30}H_{42}N_6O_2$: C, 69.47; H, 8.16; N, 16.20. Found: C, 69.19; H, 8.18; N, 16.29. **2b**: yield 83 %; yellow needles, mp 209 – 210 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS,) δ 1.98 (4H, br s), 2.13 (4H, br s), 3.13 (4H, br s), 3.41 (8H, br s), 3.79 (4H, br s), 6.20 (2H, t, J = 9.3 Hz), 6.24 (4H, br s), 6.82 (4H, br d, J = 9.3 Hz), 7.31 - 7.34 (10H, br s); IR (KBr, cm^{-1}) ν 3244, 2927, 2857, 1634, 1590, 1539, 1515, 1463, 1273, 1074, 702; MS (FAB(+), NBA, %) *m*/*z* 643 (MH^+, 33); Anal. Calcd for $C_{40}H_{46}N_6O_2$, 74.74; H, 7.21; N, 13.07. Found: C, 74.38; H, 7.32; N, 12.82. **2c**: yield 99 %; yellow needles, mp 198 – 199 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.30 (18H, s), 2.06 (8H, quint, J = 7.2 Hz), 3.30 (8H, t, J = 7.2 Hz), 3.62 (8H, t, J = 7.2 Hz), 6.02 (2H, t, J = 9.4 Hz), 6.29 (4H, d, J = 11.0 Hz), 6.79 (4H, dd, J = 11.0, 9.4 Hz); IR (KBr, cm^{-1}) ν 3222, 2927, 2856, 1614, 1588, 1548, 1515, 1464; MS (FAB(+), NBA, %) *m*/*z* 603 (MH^+, 36); Anal. Calcd for $C_{36}H_{54}N_6O_2$: C, 71.72; H, 9.03; N, 13.94. Found: C, 71.82; H, 9.11; N, 14.01.

Typical experimental procedure for the synthesis of amide-bridged TCrps (4a – 4d): To a solution of **1** (100 mg, 0.230 mmol) and 5 mol *equiv.* of DMAP in 20 mL of dry CH_2Cl_2, 1.3 mol *equiv.* of glutaryl dichloride (**3a**), adipoyl chloride (**3b**), sebacoyl chloride (**3c**) or isophthaloyl dichloride (**3d**) was added under N_2. The reaction mixture was stirred at rt for 23 h and quenched with water. The aqueous layer was extracted with CH_2Cl_2, and the organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by aluminum oxide column chromatography (eluted by EtOAc) and then recrystallized from acetonitrile or acetonitrile-CH_2Cl_2 to give amide-bridged TCrp (**4**). **4a**: yield 31 %; yellow powder, mp 176 °C (decomp); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.96 (8H, br s), 2.26 – 2.40 (6H, br m), 3.19 – 3.37 (8H, br m), 3.44 – 3.60 (8H, br m), 6.06 – 6.37 (6H, m), 6.64 – 6.77 (4H, m); IR (KBr, cm^{-1}) ν 3267, 2935, 2856, 1634, 1589, 1538, 1515, 1463, 1428, 1272; MS (FAB(+), NBA, %) *m*/*z* 531 (MH^+, 15). Anal. Calcd for $C_{31}H_{42}N_6O_2 \cdot 1/2H_2O$: C, 68.99; H, 8.03; N, 15.57. Found: C, 69.13; H, 8.02; N, 15.30. **4b**: yield 19 %; yellow powder, mp 234 °C (decomp); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.48 – 1.49 (4H, br m), 1.92 – 2.00 (8H, br m), 2.18 – 2.28 (4H, br m), 3.22 – 3.36 (8H, br m), 3.46 – 3.65 (8H, br m), 6.05 – 6.34 (6H, m), 6.68 – 6.81 (4H, m); IR (KBr, cm^{-1}) ν 3224, 2926, 2856, 1634, 1590, 1539, 1515, 1463, 1428, 1273; MS (FAB(+), NBA, %) *m*/*z* 545 (MH^+, 26). Anal. Calcd for $C_{32}H_{44}N_6O_2 \cdot 1/4H_2O$: C, 69.98; H, 8.17; N, 15.30. Found: C, 70.12; H, 8.11; N, 15.59. **4c**: yield 37 %; yellow plates, mp 191 – 192 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.10, 1.17, 1.26, 1.46, 1.64, 1.90, 2.05, 2.07, 2.28, 2.38, 2.42, 2.48, 2.91, 2.95, 3.22, 3.33 – 3.45, 3.51 – 3.67, 3.70 – 3.74, 3.91, 4.38 (total 40H, m or br m), 6.10 – 6.39 (6H, m), 6.69 – 6.83 (4H, m); IR (KBr, cm^{-1}) ν 3233, 2928, 2856, 1643, 1590, 1539, 1515, 1456, 1386, 1275, 1181, 882, 705; MS (FAB(+), NBA, %) *m*/*z* 601 (MH^+, 100). Anal. Calcd for $C_{36}H_{52}N_6O_2$: C, 71.96; H, 8.72; N, 13.99.

Found: C, 71.75; H, 8.76; N, 14.40. **4d**: yiled 18 %; yellow powder, mp 182 – 184 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.00 (8H, br s), 3.14 (4H, br s), 3.38 (4H, br s), 3.38 (4H, br s), 3.79 (4H, br s), 6.15 (2H, br s), 6.31 (4H, br s), 6.73 (4H, br s), 7.34 (4H, br s); IR (KBr, cm^{-1}) ν 3230, 2926, 2855, 1590, 1539, 1515, 1463, 1428, 1386, 1273, 705; MS (FAB(+), NBA, %) *m*/*z* 565 (MH^+, 15). Anal. Calcd for $C_{34}H_{40}N_6O_2 \cdot 1/2H_2O$: C, 71.18; H, 7.20; N, 14.65. Found: C, 70.79; H, 7.13; N, 14.41.

The reaction of TC (1) with (ethylene glycol) di-*p*-tosylate (5): A suspended solution of **1** (100 mg, 0.230 mmol), 5 mol *equiv.* of K_2CO_3 (160 mg, 1.16 mmol) and 1.3 mol *equiv.* of (ethylene glycol) di-*p*-tosylate (**5**, 111 mg, 0.299 mmol) in 20 mL of dry toluene was refluxed for 30 h under N_2 and quenched with water. The aqueous layer was extracted with CH_2Cl_2, and the organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by aluminum oxide column chromatography (eluted by EtOAc) and then recrystallized from acetonitrile or acetonitrile-CH_2Cl_2 to give 11.0 mg of ethylene-bridged TCrp (**6**) and 17.8 mg of dimer (**7**). **6**: yiled 10 %; yellow crystals, mp 178 – 179 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.84 (8H, quint, J = 5.8 Hz), 2.78 (4H, s), 2.94 (8H, t, J = 5.8 Hz), 3.27 (8H, t, J = .5.8 Hz), 6.06 (2H, t, J = 9.2 Hz), 6.16 (4H, d, J = 11.0 Hz), 6.70 (4H, dd, J = 11.0, 9.2 Hz); IR (KBr, cm^{-1}) ν 3220, 2920, 2853, 1610, 1585, 1543, 1508, 1463, 1386, 1255, 1131, 942, 697; MS (EI(+), 70 eV, %) *m*/*z* 460 ($M^{\cdot+}$, 100); Anal. Calcd for $C_{28}H_{40}N_6$: C, 73.00; H, 8.75; N, 18.24. Found: C, 72.85; H, 8.80; N, 18.31. **7**: yiled 17 %; yellow crystals, mp 187 – 190 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.93 (16H, br m), 2.66 (16H, t, J = 7.2 Hz), 2.71 (8H, s), 3.29 (16H, t, J = 6.2 Hz), 6.08 (4H, t, J = 9.2 Hz), 6.18 (8H, d, J = 11.0 Hz), 6.70 (8H, dd, J = 11.0, 9.2 Hz); IR (KBr, cm^{-1}) ν 3134, 2926, 2833, 1610, 1588, 1540, 1515, 1456, 1386, 1273, 730, 701; MS (FAB(+), NBA, %) *m*/*z* 922 (MH^+, 100); Anal. Calcd for $C_{56}H_{80}N_{12} \cdot H_2O$: C, 71.60; H, 8.80; N, 17.89. Found: C, 71.43; H, 8.63; N, 17.74.

Typical experimental procedure for the synthesis of oligo(ethylene glycol)-bridged TCrps (9a – 9d): A suspended solution of **1** (100 mg, 0.230 mmol), 5 mol *equiv.* of K_2CO_3 (160 mg, 1.16 mmol) and 1.3 mol *equiv.* of oligo(ethylene glycol) di-*p*-tosylate (**8**, 0.299 mmol) in 20 mL of dry toluene was refluxed for 30 h under N_2 and quenched with water. The aqueous layer was extracted with CH_2Cl_2, and the organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by aluminum oxide column chromatography (eluted by EtOAc) and then recrystallized from acetonitrile to give oligo(ethylene glycol)-bridged TCrp (**9**). **9a**: yield 47 %; yellow needles, mp 121 – 123 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.87 – 2.03 (8H, m), 2.61 – 2.72 (8H, m), 2.77 (4H, t, J = 6.2 Hz), 3.34 (8H, t, J = 6.2 Hz), 3.67 (4H, s), 3.72 (4H, t, J = 6.2 Hz), 6.08 (2H, t, J = 9.2 Hz), 6.21 (4H, d, J = 11.0 Hz), 6.73 (4H, dd, J = 11.0, 9.2 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 27.5 (4C), 45.1 (4C), 53.6 (4C), 54.2 (2C), 69.5 (2C), 71.2 (2C), 110 (4C), 117 (2C), 133 (4C), 153 (4C); IR (KBr, cm ^{1}) ν 3188, 2916, 2848, 1586, 1533, 1498, 1456, 1384, 1271, 1253, 1119, 993, 729; MS (EI(+), 70 eV, %) *m*/*z* 548 ($M^{\cdot+}$, 100); UV-VIS (MeCN, nm, ε) λ_{max} 264 (38300), 349 (19700), 361 (22500), 419 (14400); Anal. Calcd for $C_{32}H_{48}N_6O_2$: C, 70.04; H, 8.82; N, 15.32. Found: C, 69.92; H, 8.89; N, 15.35. **9b**: yield 47 %; yellow needles, mp 135 – 136 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.89 – 2.03 (8H, m), 2.71 (8H, t, J = 7.2 Hz), 2.80 (4H, t, J = 6.6 Hz), 3.31 (8H, t, J = 6.4 Hz), 3.62 (8H, s), 3.67 (4H, t, J = 6.6 Hz), 6.09 (2H, t, J = 9.2 Hz), 6.20 (4H, d, J = 11.0 Hz), 6.71 (4H, dd, J = 11.0, 9.2 Hz); ^{13}C NMR

(50 MHz, $CDCl_3$) δ 45.5 (4C), 27.2 (4C), 53.7 (4C), 110 (4C), 153 (4C), 133 (4C), 117 (2C), 54.1 (2C), 69.4 (2C), 70.4 (2C), 70.6 (2C); IR (KBr, cm ^{1}) ν 3177, 2941, 2856, 1588, 1539, 1507, 1457, 1386, 1273, 1121, 703; MS (FAB(+), NBA, %) *m/z* 593 (MH^+, 49); UV-VIS (MeCN, nm, ε) λ_{max} 264 (37600), 348 (20100), 360 (23000), 418 (14500); Anal. Calcd for $C_{34}H_{52}N_6O_3$: C, 68.89; H, 8.84; N, 14.18. Found: C, 68.92; H, 8.87; N, 14.27. **9c**: yield 41 %; yellow scales, mp 93.0 – 93.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.96 (8H, quint, J = 7.2 Hz), 2.73 (8H, t, J = 7.2 Hz), 2.80 (4H, t, J = 6.6 Hz), 3.30 (8H, t, J =7.2 Hz), 3.63 (12H, s), 3.69 (4H, t, J = 6.6 Hz), 6.10 (2H, t, J = 9.2 Hz), 6.20 (4H, d, J = 11.0 Hz), 6.72 (4H, dd, J = 11.0, 9.2 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 27.2 (4C), 45.5 (4C), 53.7 (4C), 54.1 (2C), 69.4 (2C), 70.4 (2C), 70.6 (2C), 110 (4C), 117 (2C), 133 (4C), 153 (4C); IR (KBr, cm ^{1}) ν 3247, 3212, 2923, 2856, 1590, 1536, 1512, 1459, 1387, 1269, 1112; MS (FAB(+), NBA, %) *m/z* 637 (MH^+, 88); UV-VIS (MeCN, nm, ε) λ_{max} 264 (38100), 348 (20000), 360 (23000), 418 (14700); Anal. Calcd for $C_{36}H_{56}N_6O_4$: C, 67.89; H, 8.86; N, 13.20. Found: C, 67.52; H, 8.85; N, 13.44. **9d**: 41%; yellow needles, mp 108 – 109 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.95 (8H, quint, J = 6.8 Hz), 2.73 (8H, t, J = 6.8 Hz), 2.79 (4H, t, J = 6.4 Hz), 3.31 (8H, t, J = 6.8 Hz), 3.63 (16H, s), 3.68 (4H, t, J = 6.4 Hz), 6.10 (2H, t, J = 9.4 Hz), 6.21 (4H, d, J = 11.0 Hz), 6.72 (4H, dd, J = 11.0, 9.4 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 27.0 (4C), 45.4 (4C), 53.3 (4C), 54.0 (2C), 69.7 (2C), 70.5 (2C), 70.6 (2C), 70.7 (2C), 70.8 (2C), 110 (4C), 117 (2C), 133 (4C), 153 (4C); IR (KBr, cm^{-1}) ν 3208, 2929, 2859, 1588, 1538, 1515, 1506, 1456, 1386, 1353, 1274, 1118, 703; MS (FAB(+), NBA, %) *m/z* 681 (MH^+, 58); UV-VIS (MeCN, nm, ε) λ_{max} 264 (38400), 348 (20300), 360 (23300), 418 (14900); Anal. Calcd for $C_{38}H_{60}N_6O_5$: C, 67.03; H, 8.88; N, 12.34. Found: C, 66.98; H, 9.01; N, 12.42.

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