

Electronic Supplementary Information (ESI)

Excitation energy migration in covalently linked perylene bisimide macrocycles

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Table of contents

1. Experimental methods	2
2. Synthesis and characterisation of PBI macrocycles 3a-d	7
3. Recycling GPC	11
4. NMR spectra.....	12
5. High resolution mass spectra	25
6. Time-resolved fluorescence decay profiles	29
7. Transient absorption spectra and power-dependent transient absorption decay profiles	30
8. References.....	31

1. Experimental methods

NMR spectroscopy. NMR spectra were recorded on a 600 MHz spectrometer and calibrated against the residual solvent peak.

Gel permeation chromatography (GPC). GPC was performed on a Shimadzu Recycling GPC system (LC-20AD prominence pump; SPD-MA20A prominence diode array detector) equipped with three preparative columns obtained from Japan Analytical Industries Co., Ltd. (JAIGEL-1H+2H+2.5H) with CHCl₃ as eluent at a flow rate of 3.5 mL min⁻¹.

Steady-state absorption and fluorescence spectra. Absorption spectra were obtained by using a UV-Vis-NIR spectrometer (Varian, Cary5000), steady-state fluorescence spectra were measured by a Hitachi model F-2500 fluorescence spectrophotometer. Steady-state excitation anisotropy spectra were obtained by changing the polarization of fluorescence detection either parallel or perpendicular to the polarization of the excitation light. The fluorescence excitation anisotropy values were then calculated as follows:

$$r = \frac{I_{VV} - G I_{VH}}{I_{VV} + 2GI_{VH}}$$

where I_{VV} (or I_{VH}) is the fluorescence excitation spectrum when the excitation light is vertically polarized and only the vertically (or horizontally) polarized portion of the fluorescence is detected, that is, the first and second subscripts represent excitation and detection polarization, respectively. The factor G is defined by I_{HV}/I_{HH} , which is equal to the ratio of the sensitivities of the detection system for vertically and horizontally polarized fluorescence.

Time-resolved fluorescence decay and anisotropy. A time-correlated single-photon-counting (TCSPC) system was used for the measurement of spontaneous fluorescence decay and fluorescence anisotropy decay. As an excitation light source, we used a mode-locked Ti:sapphire laser (Spectra

Physics, MaiTai BB) which provides ultrashort pulse (80 fs at full width half maximum, fwhm) with high repetition rate (80 MHz). This high repetition rate slows down to 1 M ~ 800 kHz by using a homemade pulse-picker. The pulse-picked output pulse was frequency-doubled by a 1 mm thickness of a BBO crystal (EKSMA). The fluorescence was collected by a microchannel plate photomultiplier (MCP-PMT, Hamamatsu, R3809U-51) with a thermoelectric cooler (Hamamatsu, C4878) connected to a TCSPC board (Becker&Hickel SPC-130). The overall instrumental response function was about 25 ps (fwhm). A vertically polarized pump pulse by a Glan-laser polarizer was irradiated to samples, and a sheet polarizer, set at an angle complementary to the magic angle (54.7°), was placed in the fluorescence collection path to obtain polarization-independent fluorescence decays. Time-resolved fluorescence anisotropy decays were obtained by changing the detection polarization on the fluorescence path to parallel or perpendicular to the polarization of the excitation pulses. The calculation of anisotropy decay was then followed by

$$r(t) = \frac{I_{VV}(t) - GI_{VH}(t)}{I_{VV}(t) + 2GI_{VH}(t)}$$

where $I_{VV}(t)$ [or $I_{VH}(t)$] is the fluorescence decay when the excitation light is vertically polarized and only the vertical (or horizontally) polarized portion of fluorescence is detected, and the first and second subscripts represent excitation and detection polarization, respectively. The factor G is defined by $I_{HV}(t)/I_{HH}(t)$, which is equal to the ratio of the sensitivities of the detection system for vertical and horizontal polarization.

Femtosecond transient absorption measurements. The femtosecond time-resolved transient absorption (TA) spectrometer pumped by a Ti:sapphire regenerative amplifier system (Quantronix, Integra-C) operating at 1 kHz repetition rate and an optical detection system. The frequency doubled 400 nm pulses had a pulse width of ~ 100 fs and an average power of 1 mW which were used as pump pulses. White light continuum (WLC) probe pulses were generated by using a sapphire

window (2 mm of thickness) and focusing a small portion of the fundamental 800 nm pulses. The time delay between pump and probe beams was carefully controlled by making the pump beam travel along a variable optical delay (Newport, ILS250). Intensities of the spectrally dispersed WLC probe pulses are monitored by miniature spectrograph (OceanOptics, USB2000+). To obtain the time-resolved transient absorption difference signal (ΔA) at a specific time, the pump pulses were chopped at 25 Hz and absorption spectra intensities were saved alternately with or without pump pulse. Typically, 6000 pulses excite samples to obtain the TA spectra at a particular delay time. The polarization angle between pump and probe beam was set at the magic angle (54.7°) in order to prevent polarization-dependent signals. Cross-correlation fwhm in pump-probe experiments was less than 200 fs and chirp of WLC probe pulses was measured to be 800 fs in the 400-800 nm region. To minimize chirp, all reflection optics in probe beam path and 2 mm path length of quartz cell were used. The three-dimensional data sets of ΔA versus time and wavelength were subjected to singular value decomposition and global fitting to obtain the kinetic time constants and their associated spectra using Surface Explorer software.

Femtosecond transient absorption anisotropy decay. A dual-beam femtosecond time-resolved transient absorption (TA) spectrometer consisted of two independently tuneable homemade optical parametric amplifiers (OPA) pumped by a regeneratively amplified Ti:sapphire laser system (Spectra-Physics, Hurricane-X) operating at 5 kHz repetition rate and an optical detection system. The OPA was based on noncollinearly phase-matching geometry, which was easily color-tuned by controlling optical delay between white light continuum seed pulses (450-1400 nm) and visible pump pulses (400 nm) produced by using a sapphire window and BBO crystal, respectively. The generated visible OPA pulses had a pulse width of ~ 35 fs and an average power of 10 mW at 5 kHz repetition rate in the range of 500-700 nm after a fused-silica prism compressor. Two OPA pulses were used as the pump and probe pulses, respectively, for TA measurements. The probe beam was split into two parts. The one part of the probe beam was overlapped with the pump beam at the sample to monitor the transient (signal), while the other part of the probe beam was passed through

the sample without overlapping the pump beam to compensate the fluctuation of probe beam. The time delay between pump and probe beams was carefully controlled by making the pump beam travel along a variable optical delay (Newport, ILS250). To obtain the time-resolved transient absorption difference signal at specific wavelength, the monitoring wavelength was selected by using a narrow interface filter (fwhm \sim 10nm). By chopping the pump pulses at 47 Hz, the modulated probe pulses as well as the reference pulses were detected by two separated photodiodes (New Focus, Femtowatt Photoreceiver). The modulated signals of the probe pulses were measured by a gated integrator (SRS, SR250) and a lock-in amplifier (EG&G, DSP7265) and stored in a personal computer for further signal processing. In general experimental conditions, time resolutions of less than 50 fs were achieved. For time-resolved transient absorption anisotropy (TAA) measurement, both I_{\parallel} and I_{\perp} signals were collected simultaneously by combination of polarizing beam splitter cube and dual lock-in amplifiers as the following equation:

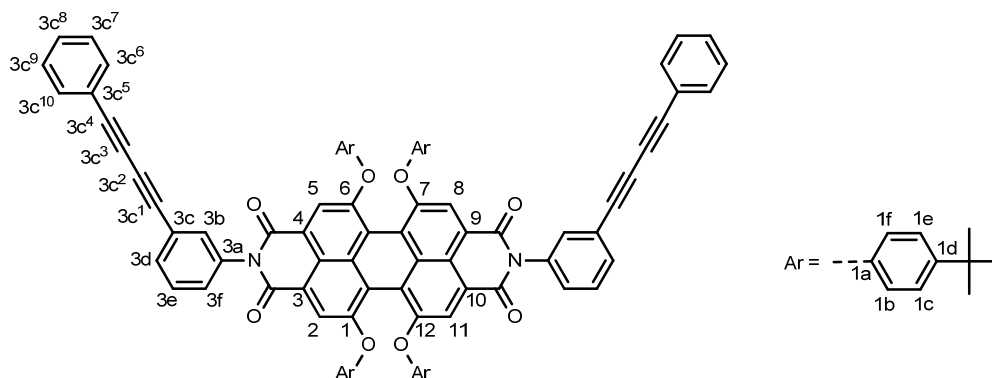
$$r(t) = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}}$$

where I_{\parallel} and I_{\perp} represent TA signals with the polarization of the pump and probe pulses being mutually parallel and perpendicular, respectively. The pump pulses were set to vertical polarization and that of probe pulse was set to 45° with respect to the pump pulse by using Glan-laser polarisers and half-wave plates. After the probe pulse passes through the sample cell, it was split by a polarizing beam splitter cube and then detected by two separated photodiodes. Two gated integrators and two lock-in amplifiers record the signal simultaneously within a single scan. As a standard, anisotropy measurement showed a clean single-exponential decay with reorientational relaxation times of 120 ps and the initial anisotropy $r(0)$ value of 0.39 for rhodamine 6G dye in methanol, which are well-matched in other reference.² For all TAA measurements, the wavelength of the pump and probe pulse was set to 580 nm with an average power of less than 40 μ W and a thin absorption cell with a path length of 1 mm was used to eliminate additional chirping.

Computational methods. Quantum mechanical calculations were carried out with Gaussian 03 program suit.³ Geometry optimizations were performed by density functional theory (DFT) method with Becke's three-parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP) employing a basis set consisting of 6-31G(d).

2. Synthesis and characterization of PBI macrocycles 3a-d

Reference compound PBI monomer 2:

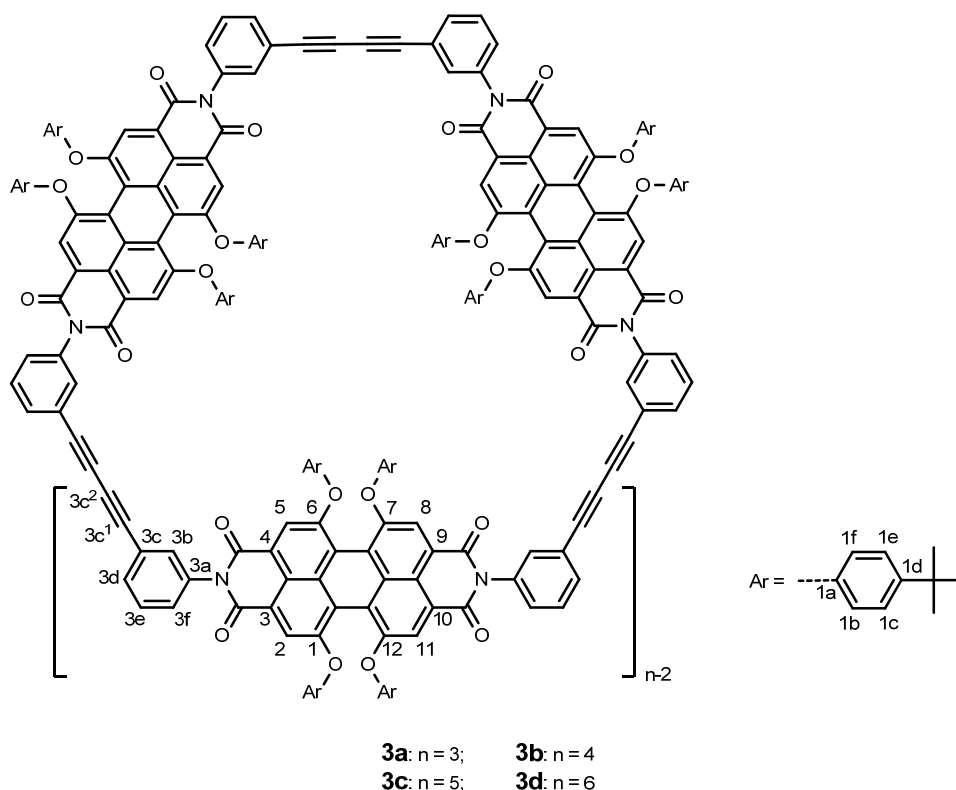


A solution of perylene bisimide **1**¹ (31.0 mg, 26.0 μmol), phenyl acetylene (43.0 mg, 0.42 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (1.80 mg, 2.60 μmol) and copper iodide (0.50 mg, 2.60 μmol) in distilled dichloromethane (50 mL) was heated to 40 °C. Then diisopropylamine (10 mL) was added at ambient atmosphere and the reaction mixture was stirred for 35 minutes at this temperature. The solvent was removed at a rotary evaporator and the reaction mixture was purified by column chromatography with dichloromethane/*n*-hexane (7:3 vol%) to give compound **2** (25 mg, 69%) as a dark red powder.

¹H NMR (600 MHz, CD_2Cl_2 , 298 K): δ 8.18 (s, 4H; 2-H, 5-H, 8-H, 11-H), 7.63–7.62 (m, 2H; 3d-H), 7.54–7.50 (m, 6H; 3e-H, 3c⁶-H, 3c¹⁰-H), 7.44 (t, 2H; ⁴J = 1.8 Hz; 3b-H), 7.42–7.38 (m, 2H; 3c⁸-H), 7.37–7.34 (m, 4H; 3c⁷-H, 3c⁹-H), 7.32–7.30 (m, 2H; 3f-H), 7.28–7.26 (m., 8H; 1c-H, 1e-H), 6.86–6.83 (m, 8H; 1b-H, 1f-H), 1.28 (s, 36H; C(CH₃)₃); ¹³C NMR (150 MHz, CD_2Cl_2 , 298 K): δ 163.7 (C=O), 156.4 (1-C, 6-C, 7-C, 12-C), 153.6 (1a-C), 148.0 (1d-C), 136.3 (3a-C), 133.7 (Per-C), 133.2 (3b-C, 3d-C), 133.0 (3c⁶-C, 3c¹⁰-C), 130.5 (3f-C), 130.0 (3e-C, 3c⁸-C), 129.0 (3c⁷-C, 3c⁹-C), 127.2 (1c-C, 1e-C), 123.4 (3c-C), 123.0 (Per-C), 121.9 (3c⁵-C), 121.5 (Per-C), 120.8 (2-C, 5-C, 8-C, 11-C), 120.3 (Per-C), 119.6 (1b-C, 1f-C), 82.5 (3c⁴-C), 80.7 (3c¹-C), 75.2 (3c²-C), 74.0 (3c³-C), 34.8

($C(CH_3)_3$), 31.7 ($C(CH_3)_3$); MS (MALDI, matrix: DCTP, pos. mode): $m/z = 1383.570 [M]^+$ (calcd for $C_{96}H_{74}N_2O_8$ 1383.623); HRMS (ESI, $CHCl_3$ /acetonitrile 1:1, pos. mode): m/z 1384.5547 $[M+H]^+$ (calcd for $C_{96}H_{75}N_2O_8$ 1384.5552).

Macrocycles **3a-d**:



To a solution of perylene bisimide **1**¹ (340 mg, 0.287 mmol), $Pd(PPh_3)_2Cl_2$ (100 mg, 0.14 mmol) and copper iodide (40.0 mg, 0.21 mmol) in distilled dichloromethane (1.8 L) was added diisopropylamine (200 mL) at ambient atmosphere. Afterwards, the reaction mixture was stored in the freezer at $-28\text{ }^\circ\text{C}$ for four days. The solvent was removed at a rotary evaporator and the reaction mixture was filtrated through a silica gel pad with dichloromethane to remove residual reagents and parts of oligomeric side products. The obtained product mixture (200 mg, 59%) was further purified by recycling GPC and the trimer **3a** (31 mg, 8.7 μmol , 9.1%), tetramer **3b** (18 mg, 3.8 μmol , 5.3%),

pentamer **3c** (11 mg, 1.9 μmol , 3.2%) and hexamer **3d** (9 mg, 1.3 μmol , 2.7%) were isolated after in pure form eight cycles (see Fig. S1).

Compound **3a**¹ (trimer): ¹H NMR (600 MHz, CD₂Cl₂, 298 K): δ 8.16 (s, 12H; 2-H, 5-H, 8-H, 11-H), 7.62–7.60 (m, 6H; 3d-H), 7.52–7.49 (m, 6H; 3e-H), 7.41–7.40 (m, 6H; 3b-H), 7.33–7.31 (m, 6H; 3f-H), 7.26–7.24 (m, 24H; 1c-H, 1e-H), 6.83–6.81 (m, 24H; 1b-H, 1f-H), 1.27 (s, 108H; C(CH₃)₃); ¹³C NMR (150 MHz, CD₂Cl₂, 298 K): δ 163.6 (C=O), 156.4 (1-C, 6-C, 7-C, 12-C), 153.6 (1a-C), 147.9 (1d-C), 136.3 (3a-C), 133.6 (Per-C), 133.5 (3b-C), 132.9 (3d-C), 130.6 (3f-C), 130.0 (3e-C), 127.2 (1c-C, 1e-C), 123.2 (3c-C), 123.0 (Per-C), 121.5 (Per-C), 120.8 (2-C, 5-C, 8-C, 11-C), 120.3 (Per-C), 119.6 (1b-C, 1f-C), 81.1 (3c¹-C), 75.0 (3c²-C), 34.8 (C(CH₃)₃), 31.7 (C(CH₃)₃); MS (MALDI, matrix: DCTP, pos. mode): m/z = 3543.348 [M]⁺ (calcd for C₂₄₀H₁₉₂N₆O₂₄ 3543.406); HRMS (ESI, CHCl₃/acetonitrile 1:1, pos. mode): m/z 1772.7022 [M+2H]²⁺ (calcd for C₂₄₀H₁₉₄N₆O₂₄ 1772.7106).

Compound **3b** (tetramer): ¹H NMR (600 MHz, CD₂Cl₂, 298 K): δ 8.18 (s, 16H; 2-H, 5-H, 8-H, 11-H), 7.62–7.61 (m, 8H; 3d-H), 7.52–7.49 (m, 8H; 3e-H), 7.43–7.42 (m, 8H; 3b-H), 7.32–7.30 (m, 8H; 3f-H), 7.27–7.26 (m, 32H; 1c-H, 1e-H), 6.86–6.84 (m, 32H; 1b-H, 1f-H), 1.27 (s, 144H; C(CH₃)₃); ¹³C NMR (150 MHz, CD₂Cl₂, 298 K): δ 163.7 (C=O), 156.4 (1-C, 6-C, 7-C, 12-C), 153.7 (1a-C), 148.0 (1d-C), 136.3 (3a-C), 133.7 (Per-C), 133.3 (3b-C, 3d-C), 130.6 (3f-C), 130.0 (3e-C), 127.2 (1c-C, 1e-C), 123.2 (3c-C), 123.1 (Per-C), 121.5 (Per-C), 120.8 (2-C, 5-C, 8-C, 11-C), 120.3 (Per-C), 119.6 (1b-C, 1f-C), 81.2 (3c¹-C), 75.0 (3c²-C), 34.8 (C(CH₃)₃), 31.7 (C(CH₃)₃); MS (MALDI, matrix: DCTP, pos. mode): m/z = 4724.610 [M]⁺ (calcd for C₃₂₀H₂₅₆N₈O₃₂ 4724.875); HRMS (ESI, CH₂Cl₂, pos. mode): m/z 2363.4441 [M+2H]²⁺ (calcd for C₃₂₀H₂₅₈N₈O₃₂ 2363.4448).

Compound **3c** (pentamer): ¹H NMR (600 MHz, CD₂Cl₂, 298 K): δ 8.18 (s, 20H; 2-H, 5-H, 8-H, 11-H), 7.62–7.60 (m, 10H; 3d-H), 7.51–7.49 (m, 10H; 3e-H), 7.43–7.42 (m, 10H; 3b-H), 7.31–7.30 (m, 10H; 3f-H), 7.27–7.26 (m, 40H; 1c-H, 1e-H), 6.86–6.84 (m, 40H; 1b-H, 1f-H), 1.27 (s, 180H; C(CH₃)₃); ¹³C NMR (150 MHz, CD₂Cl₂, 298 K): δ 163.7 (C=O), 156.4 (1-C, 6-C, 7-C, 12-C), 153.6 (1a-C), 148.0 (1d-C), 136.3 (3a-C), 133.7 (Per-C), 133.3 (3b-C), 133.1 (3d-C), 130.6 (3f-C), 130.0

(3e-C), 127.2 (1c-C, 1e-C), 123.2 (3c-C), 123.1 (Per-C), 121.5 (Per-C), 120.8 (2-C, 5-C, 8-C, 11-C), 120.4 (Per-C), 119.6 (1b-C, 1f-C), 81.2 (3c¹-C), 75.0 (3c²-C), 34.8 (C(CH₃)₃), 31.7 (C(CH₃)₃); MS (MALDI, matrix: DCTP, pos. mode): $m/z = 5906.600 [M]^+$ (calcd for C₄₀₀H₃₂₀N₁₀O₄₀ 5906.345); HRMS (ESI, CHCl₃/acetonitrile 1:1, pos. mode): $m/z 2954.1725 [M+2H]^{2+}$ (calcd for C₄₀₀H₃₂₂N₁₀O₄₀ 2954.1795).

Compound **3d** (hexamer): ¹H NMR (600 MHz, CD₂Cl₂, 298 K): δ 8.16 (s, 24H; 2-H, 5-H, 8-H, 11-H), 7.62–7.60 (m, 12H; 3d-H), 7.51–7.47 (m, 12H; 3e-H), 7.43–7.42 (m, 12H; 3b-H), 7.32–7.29 (m, 12H; 3f-H), 7.28–7.24 (m, 48H; 1c-H, 1e-H), 6.87–6.82 (m, 48H; 1b-H, 1f-H), 1.27 (s, 216H; C(CH₃)₃); ¹³C NMR (150 MHz, CD₂Cl₂, 298 K): δ 163.6 (C=O), 156.4 (1-C, 6-C, 7-C, 12-C), 153.6 (1a-C), 147.9 (1d-C), 136.3 (3a-C), 133.6 (Per-C), 133.3 (3b-C), 133.1 (3d-C), 130.6 (3f-C), 130.0 (3e-C), 127.2 (1c-C, 1e-C), 123.2 (3c-C), 123.0 (Per-C), 121.5 (Per-C), 120.8 (2-C, 5-C, 8-C, 11-C), 120.3 (Per-C), 119.6 (1b-C, 1f-C), 81.2 (3c¹-C), 75.0 (3c²-C), 34.8 (C(CH₃)₃), 31.7 (C(CH₃)₃); MS (MALDI, matrix: DCTP, pos. mode): $m/z = 7088.302 [M]^+$ (calcd for C₄₈₀H₃₈₄N₁₂O₄₈ 7087.814); HRMS (ESI, CHCl₃/THF 1:1, pos. mode): $m/z 3566.9019 [M+2Na]^{2+}$ (calcd for C₄₈₀H₃₈₄N₁₂Na₂O₄₈ 3566.8963).

3. Recycling GPC

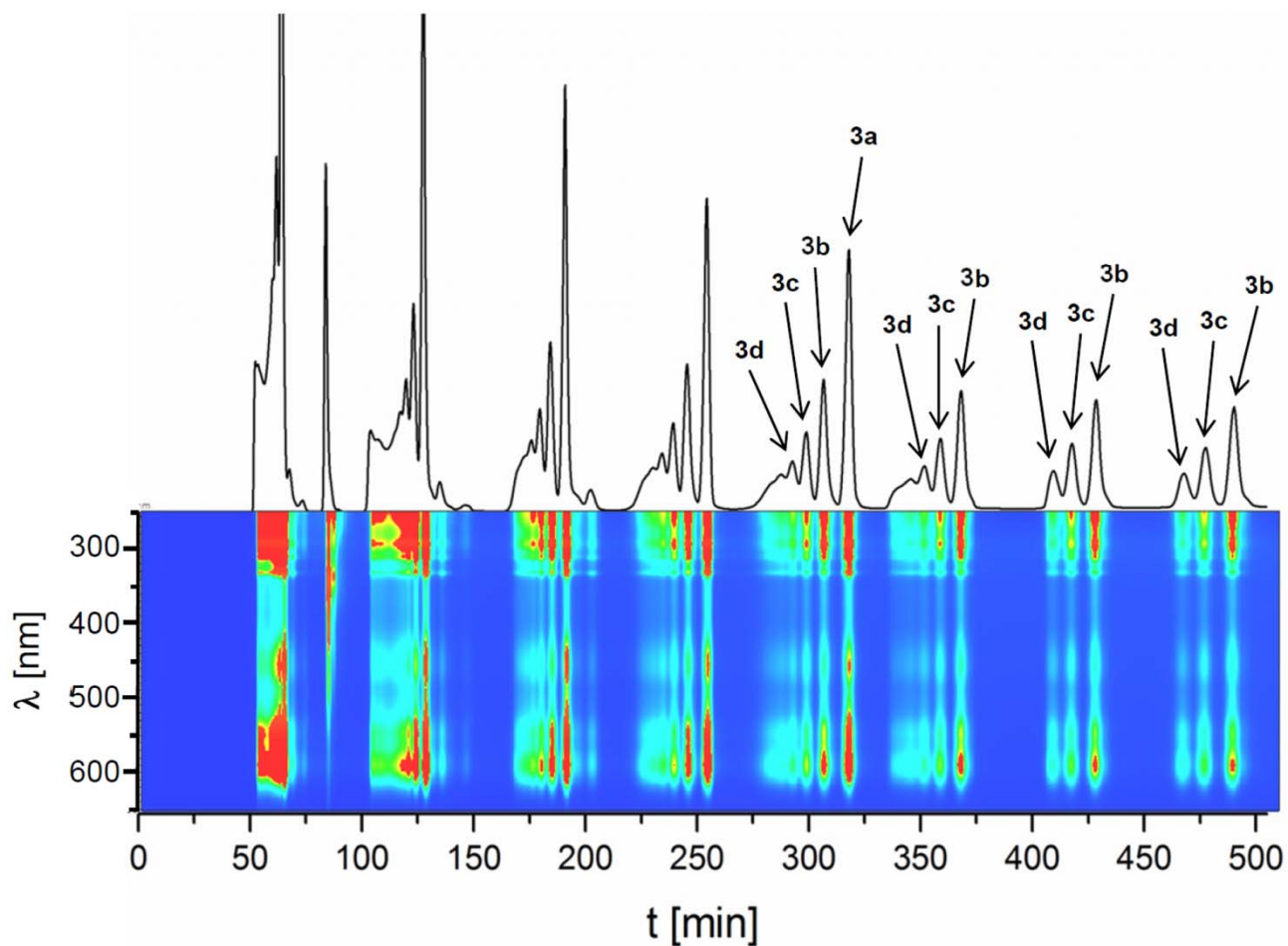


Fig. S1 Recycling GPC traces of the mixture of macrocycles **3a-d** (top: cross-section with detection at 490 nm). Cyclic trimer **3a**, tetramer **3b**, pentamer **3c** and hexamer **3d** were obtained in pure form after 500 minutes. Residual reagents and oligomeric side products were cut off during the recycling process. Pure cyclic trimer **3a** could be collected already after 314-321 minutes.

4. NMR spectra

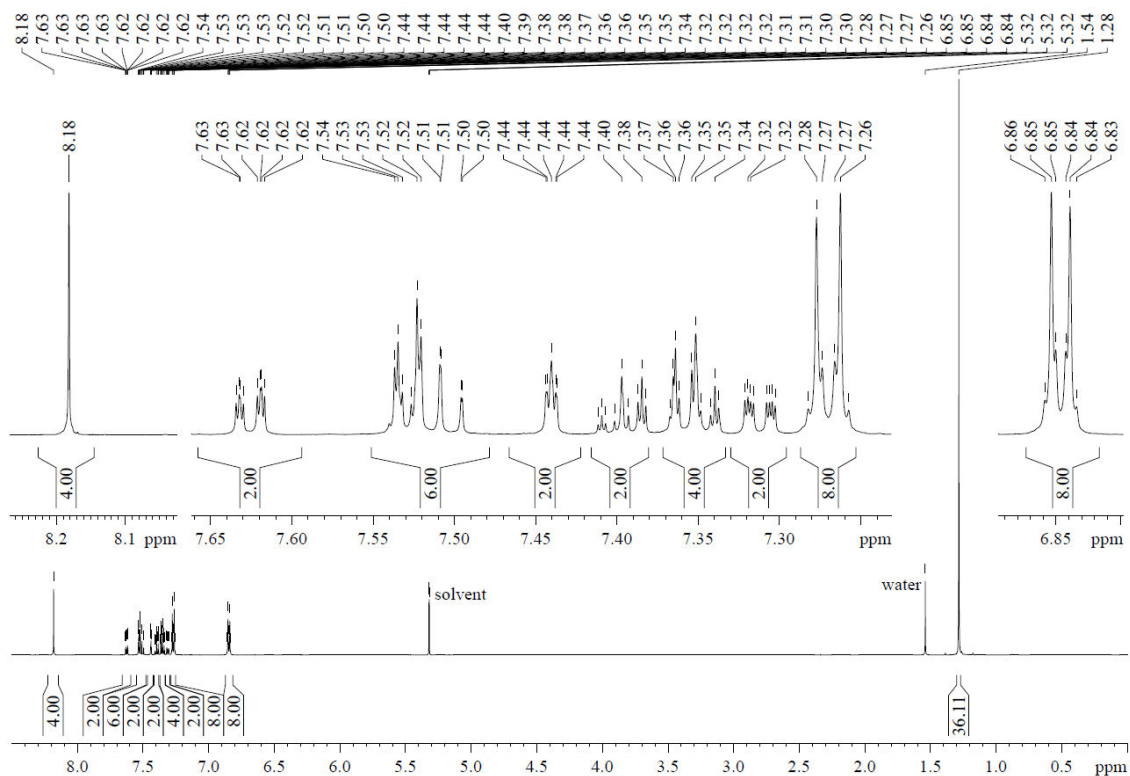


Fig. S2 ^1H NMR spectrum (600 MHz, CD_2Cl_2 , 298 K) of reference compound **2**.

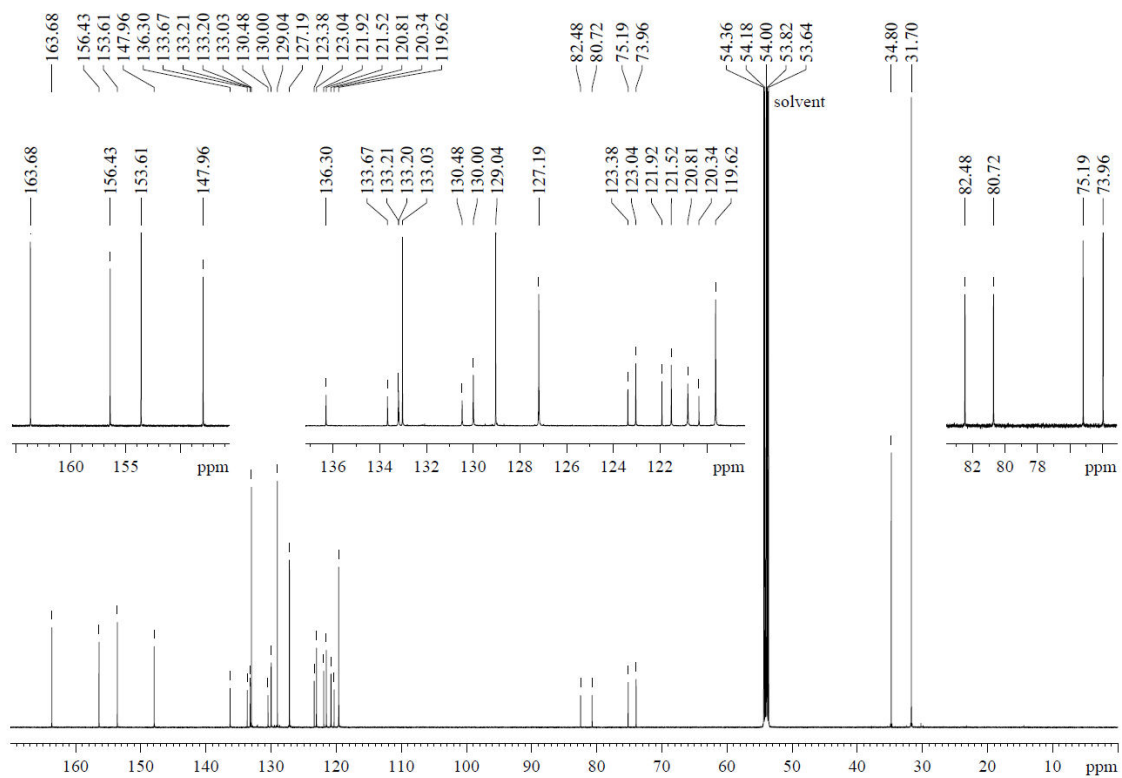


Fig. S3 ^{13}C NMR spectrum (150 MHz, CD_2Cl_2 , 298 K) of reference compound **2**.

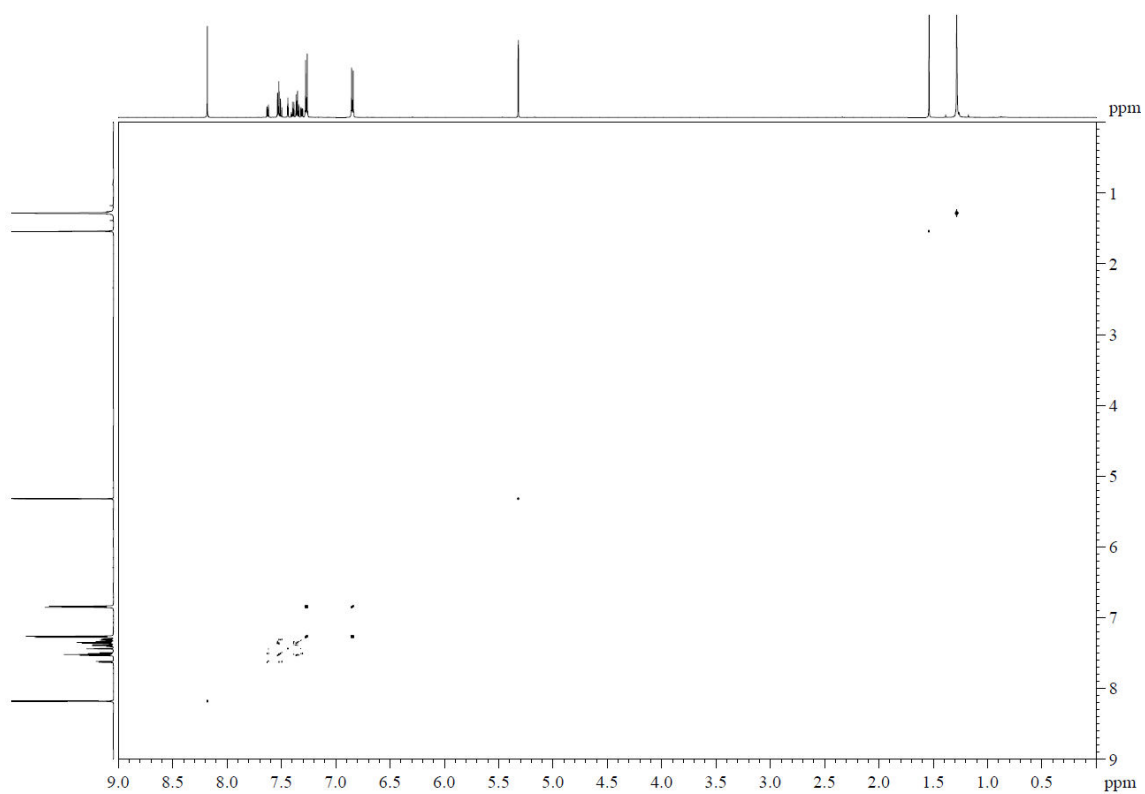


Fig. S4 (^1H , ^1H) COSY NMR spectrum of reference compound **2**.

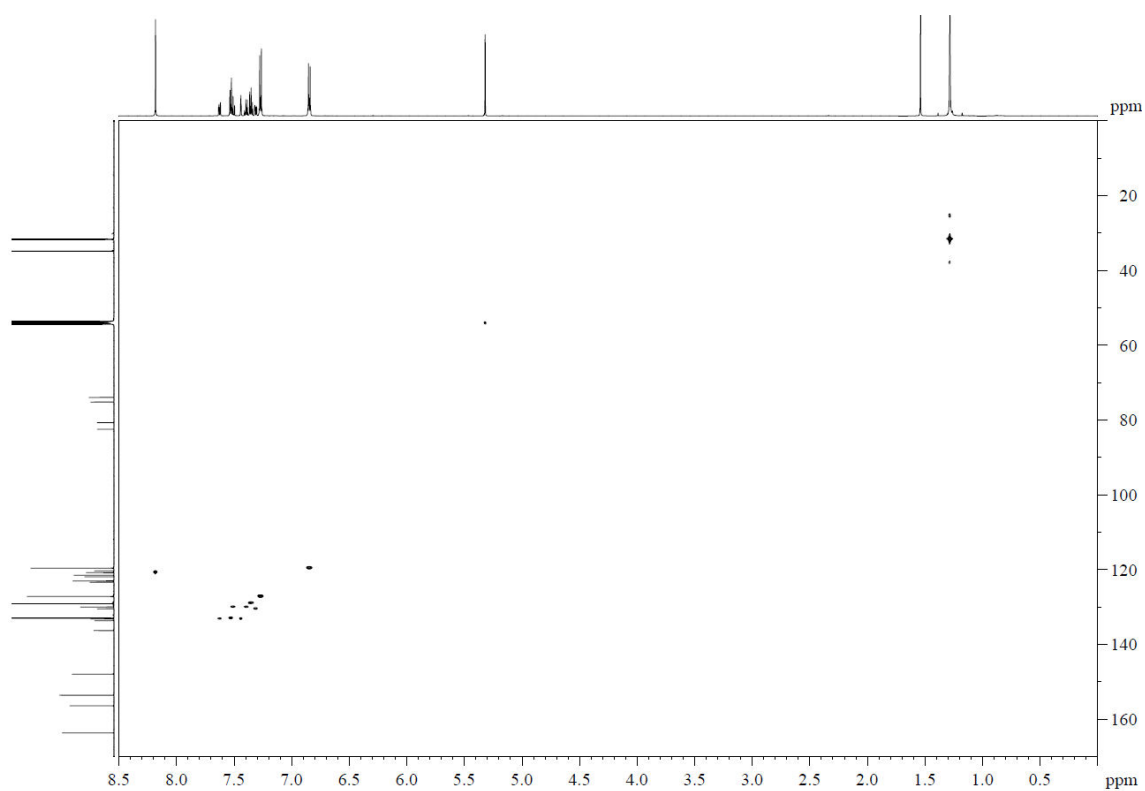


Fig. S5 (^1H , ^{13}C) HSQC NMR spectrum of reference compound **2**.

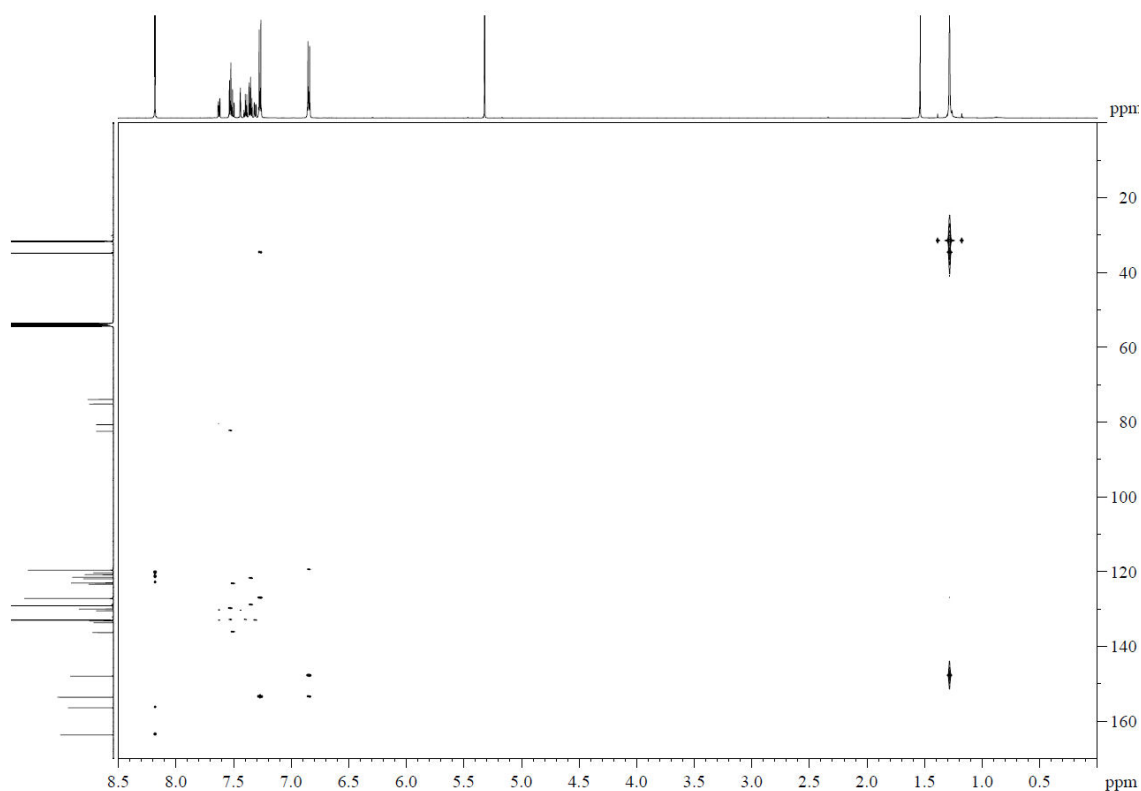


Fig. S6 (^1H , ^{13}C) HMBC NMR spectrum of reference compound **2**.

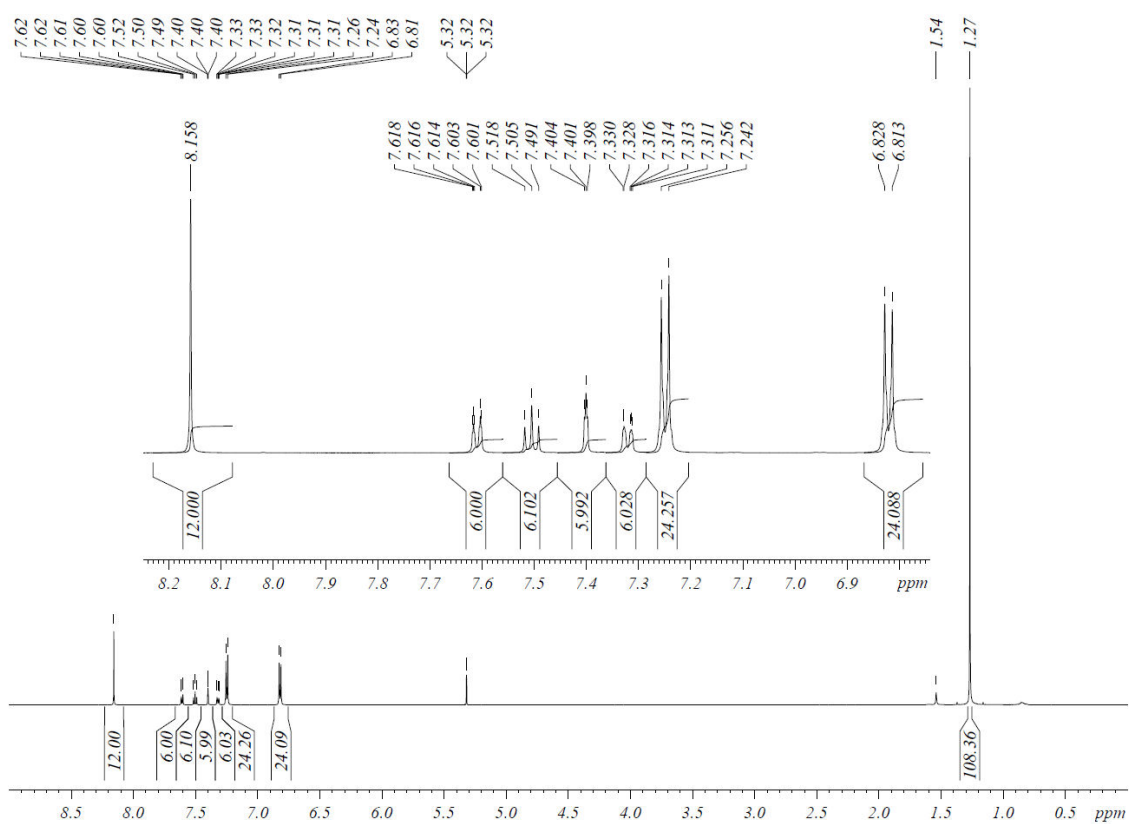


Fig. S7 ^1H NMR spectrum (600 MHz, CD_2Cl_2 , 298 K) of trimer **3a**.

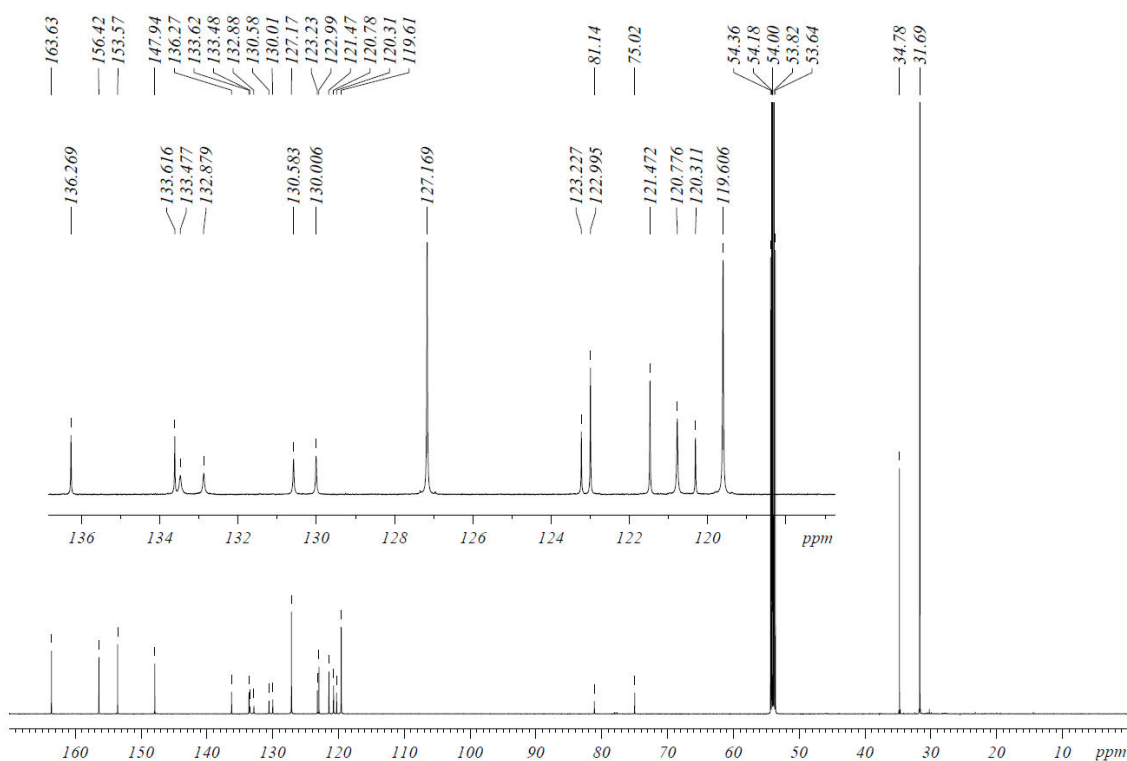


Fig. S8 ^{13}C NMR spectrum (150 MHz, CD_2Cl_2 , 298 K) of trimer **3a**.

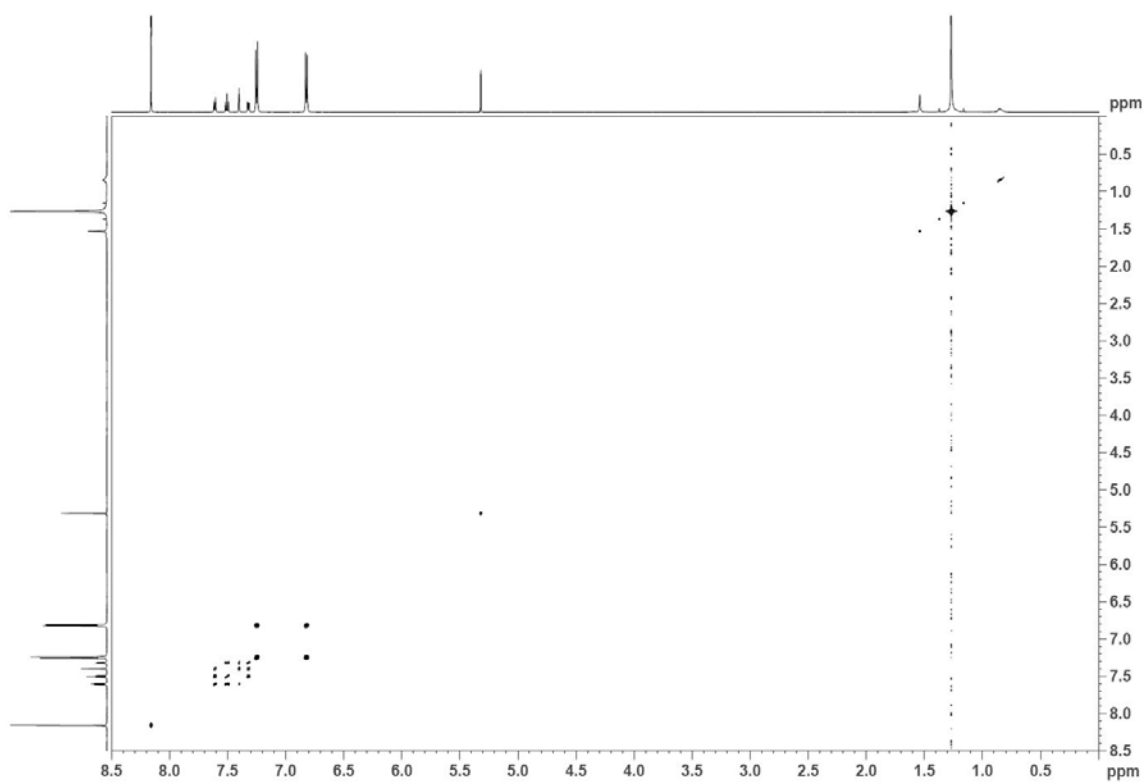


Fig. S9 (^1H , ^1H) COSY NMR spectrum of trimer **3a**.

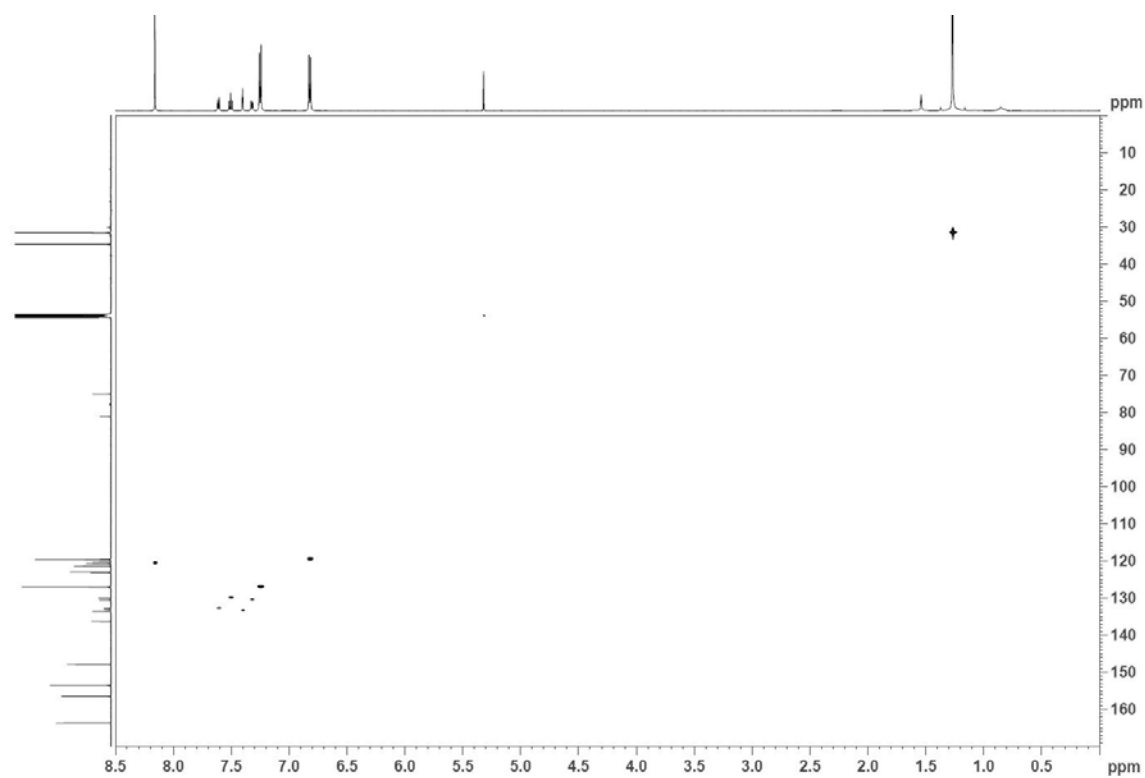


Fig. S10 (^1H , ^{13}C) HSQC NMR spectrum of trimer **3a**.

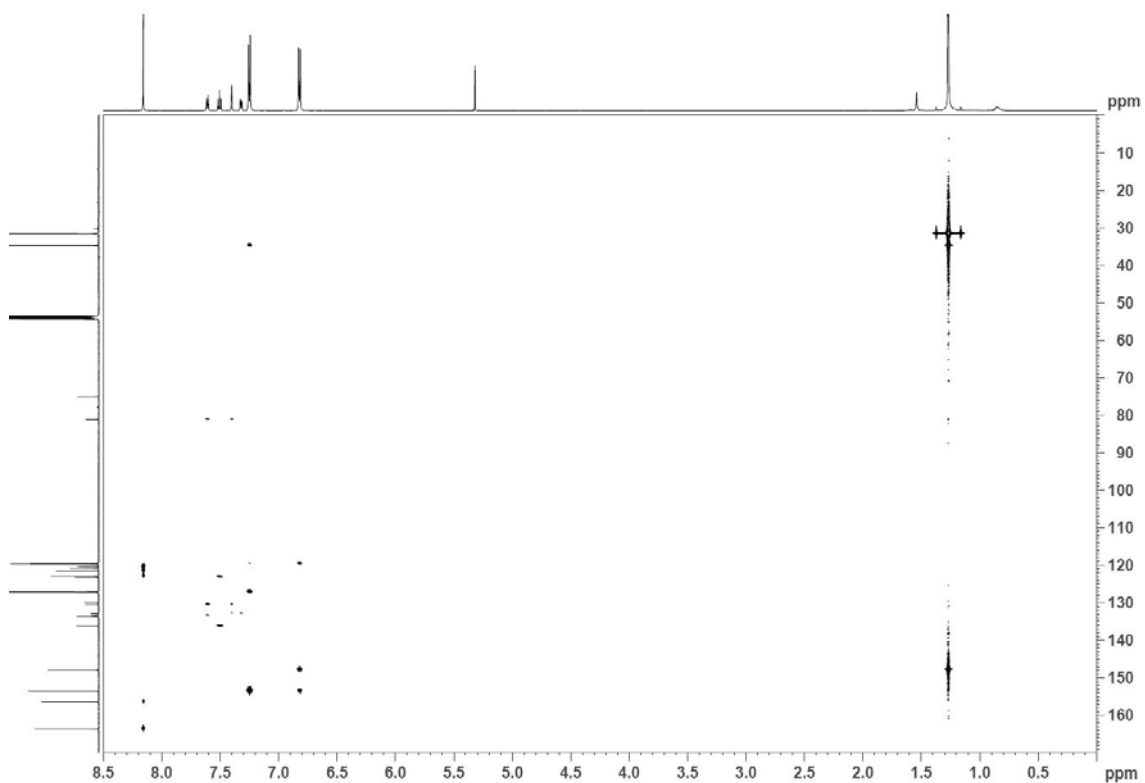


Fig. S11 (^1H , ^{13}C) HMBC NMR spectrum of trimer **3a**.

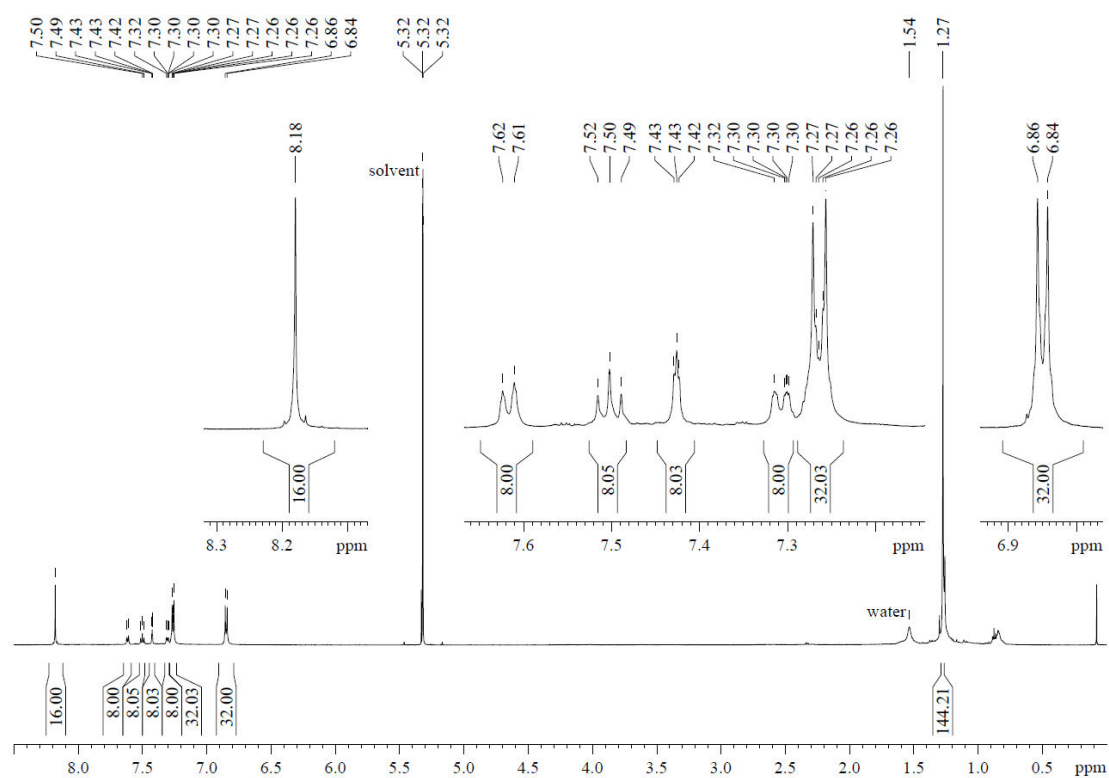


Fig. S12 ¹H NMR spectrum (600 MHz, CD₂Cl₂, 298 K) of tetramer **3b**.

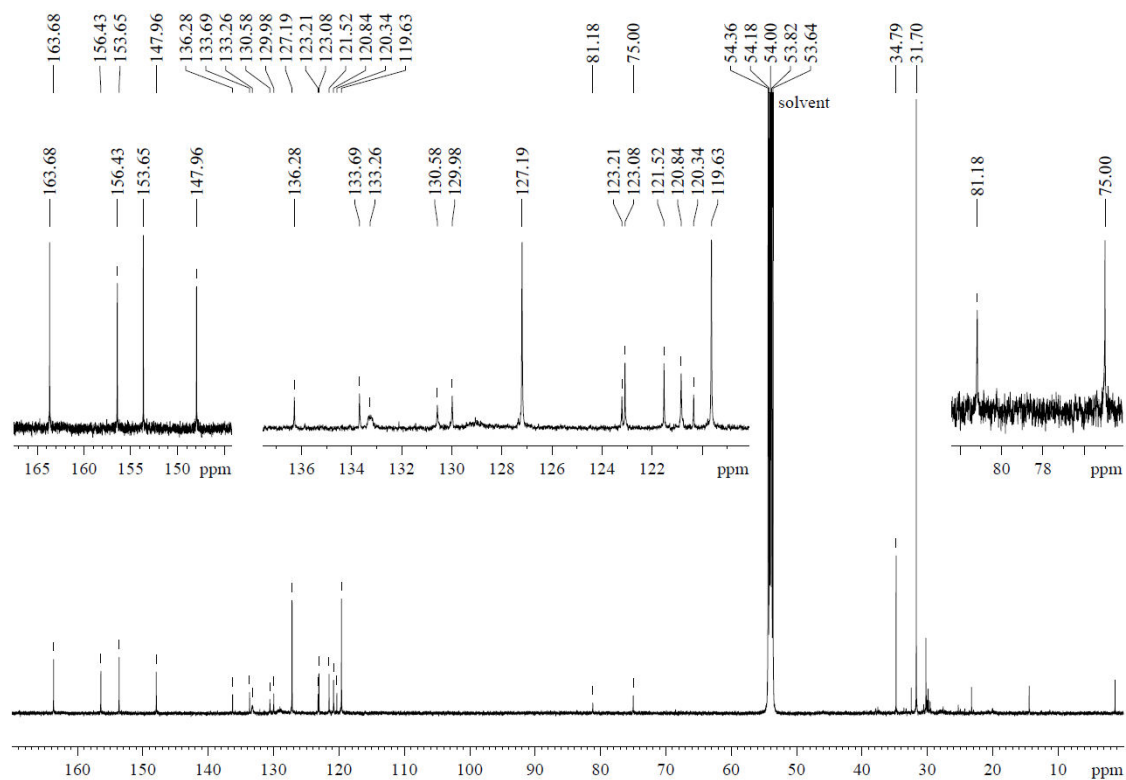


Fig. S13 ¹³C NMR spectrum (150 MHz, CD₂Cl₂, 298 K) of tetramer **3b**.

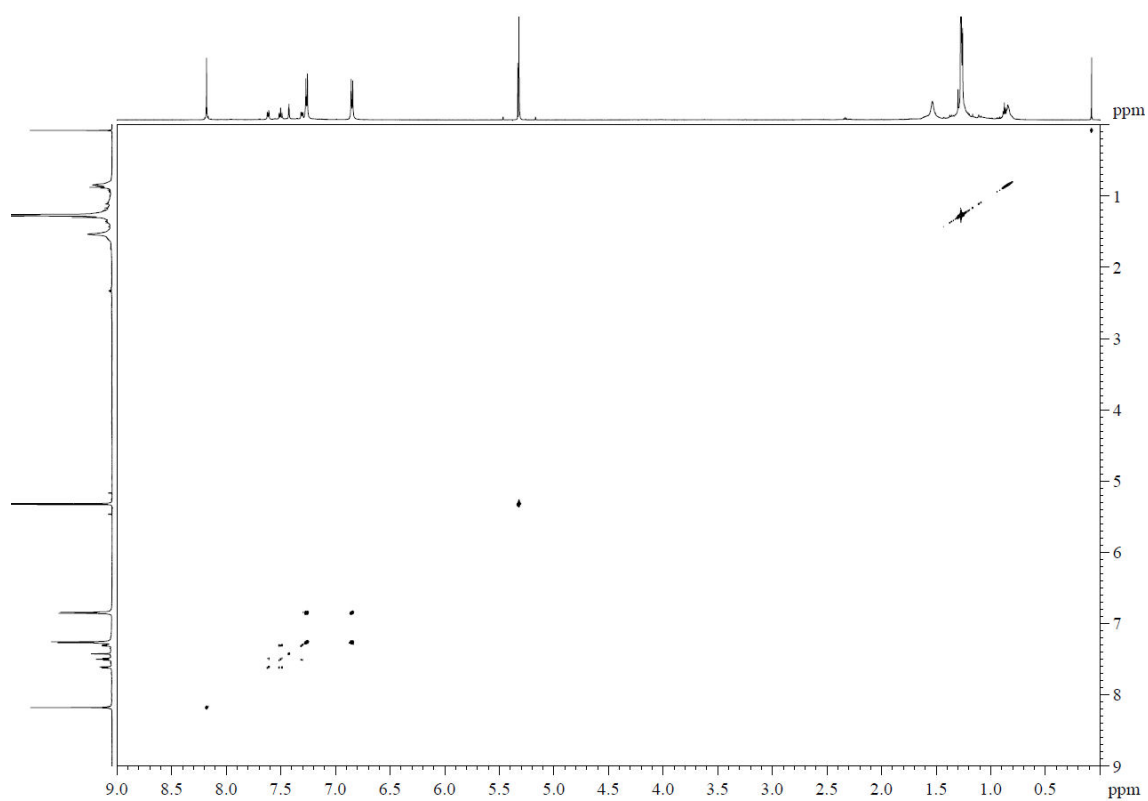


Fig. S14 (^1H , ^1H) COSY NMR spectrum of tetramer **3b**.

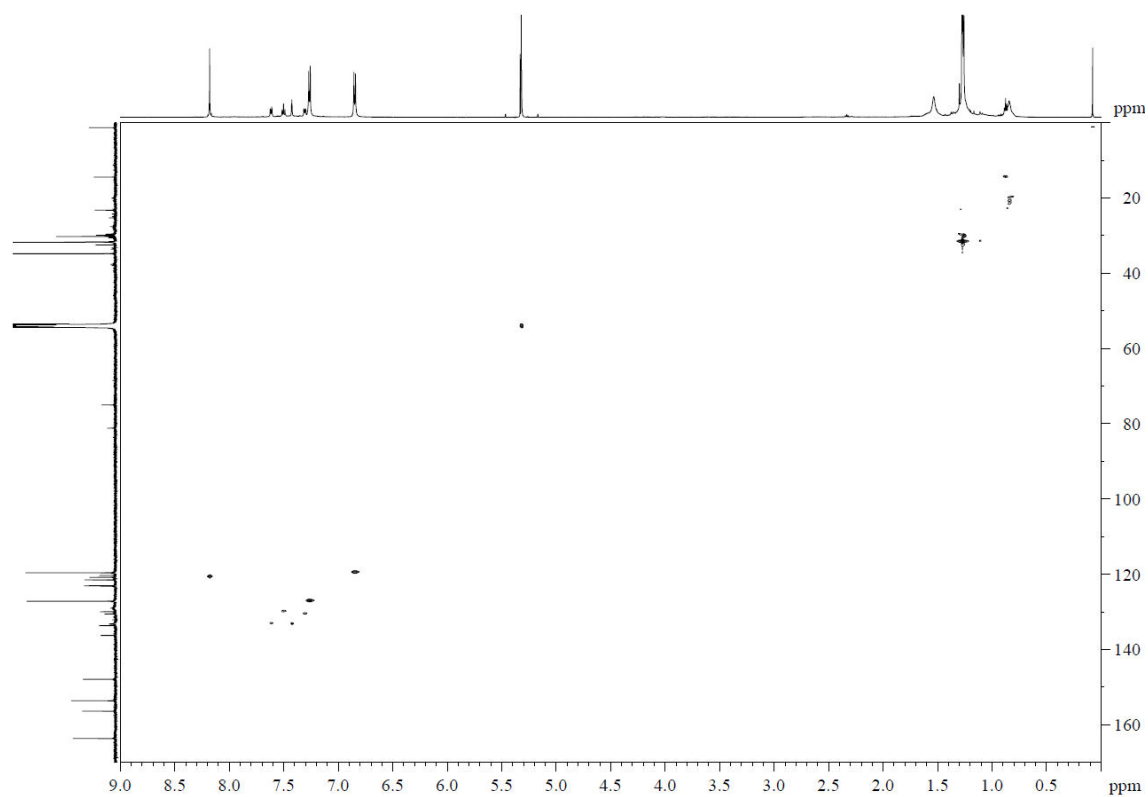


Fig. S15 (^1H , ^{13}C) HSQC NMR spectrum of tetramer **3b**.

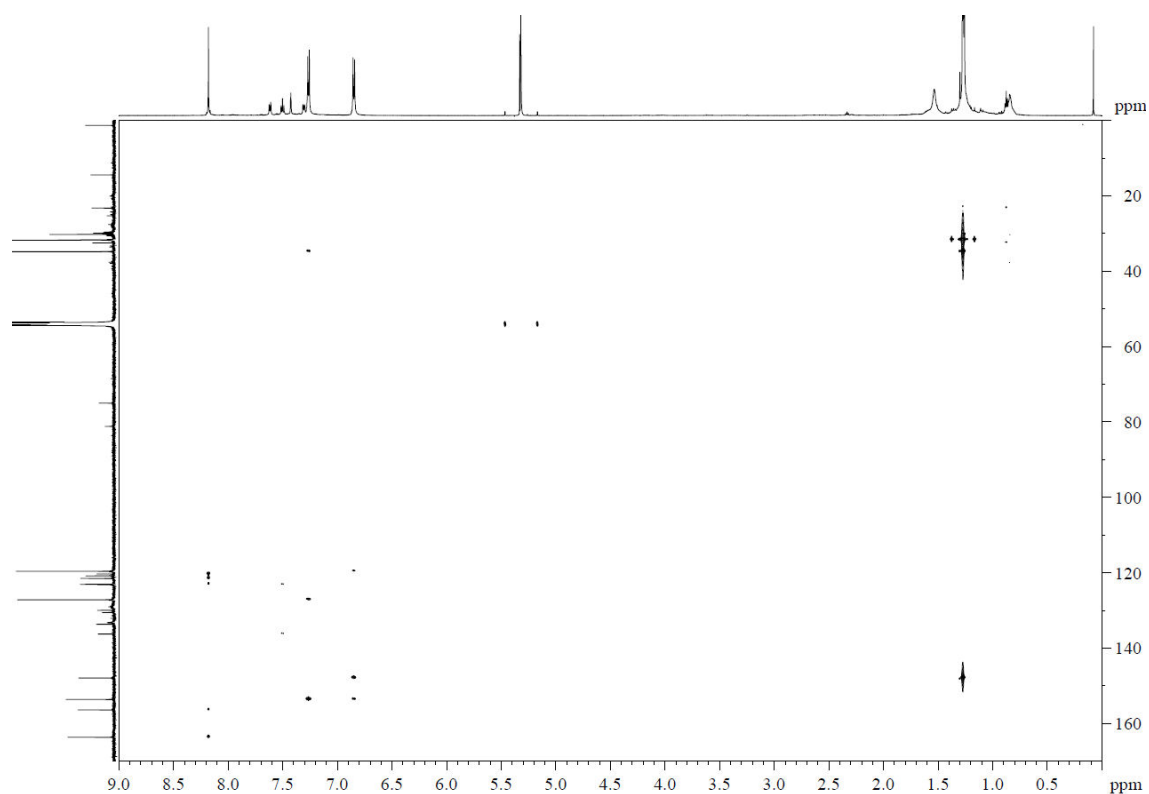


Fig. S16 (^1H , ^{13}C) HMBC NMR spectrum of tetramer **3b**.

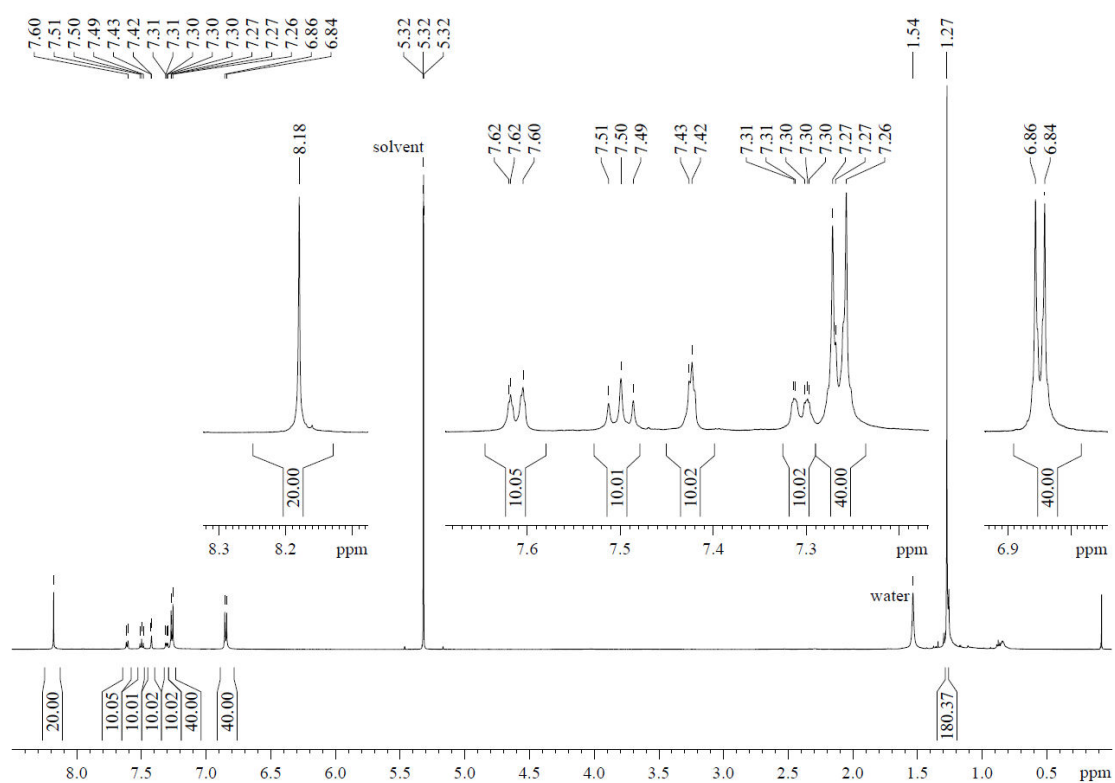


Fig. S17 ^1H NMR spectrum (600 MHz, CD_2Cl_2 , 298 K) of pentamer **3c**.

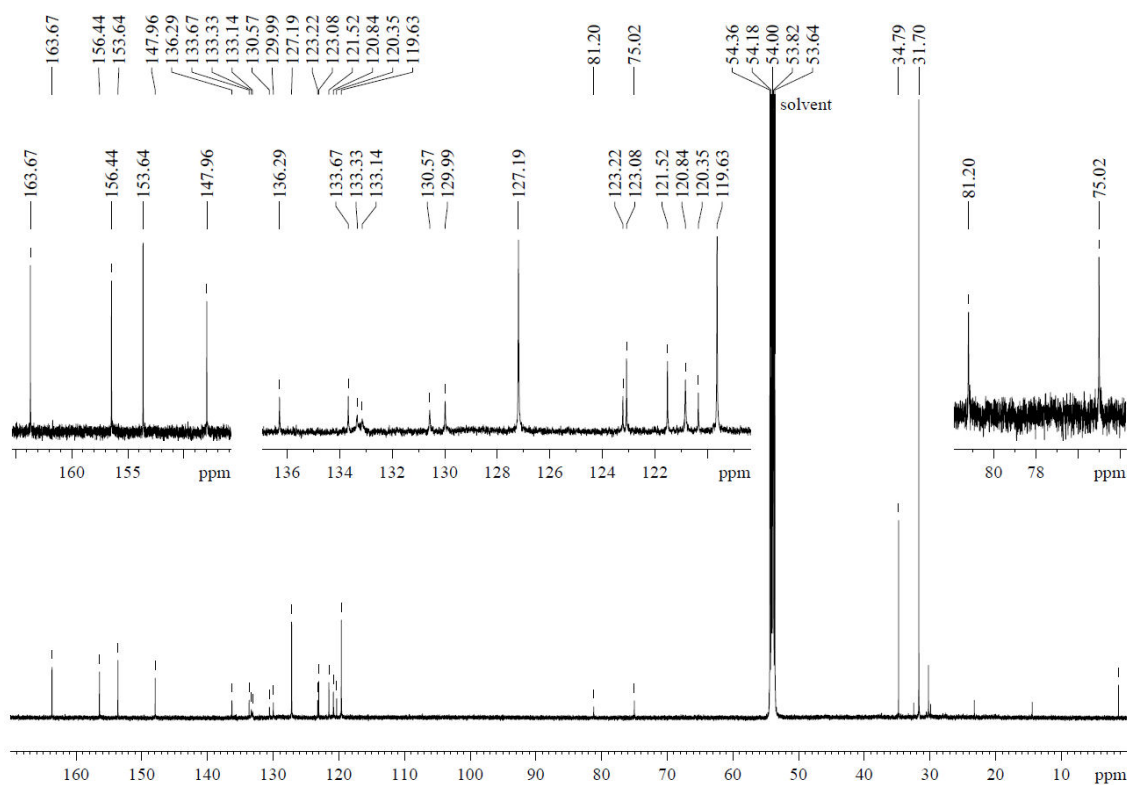


Fig. S18 ¹³C NMR spectrum (150 MHz, CD₂Cl₂, 298 K) of pentamer **3c**.

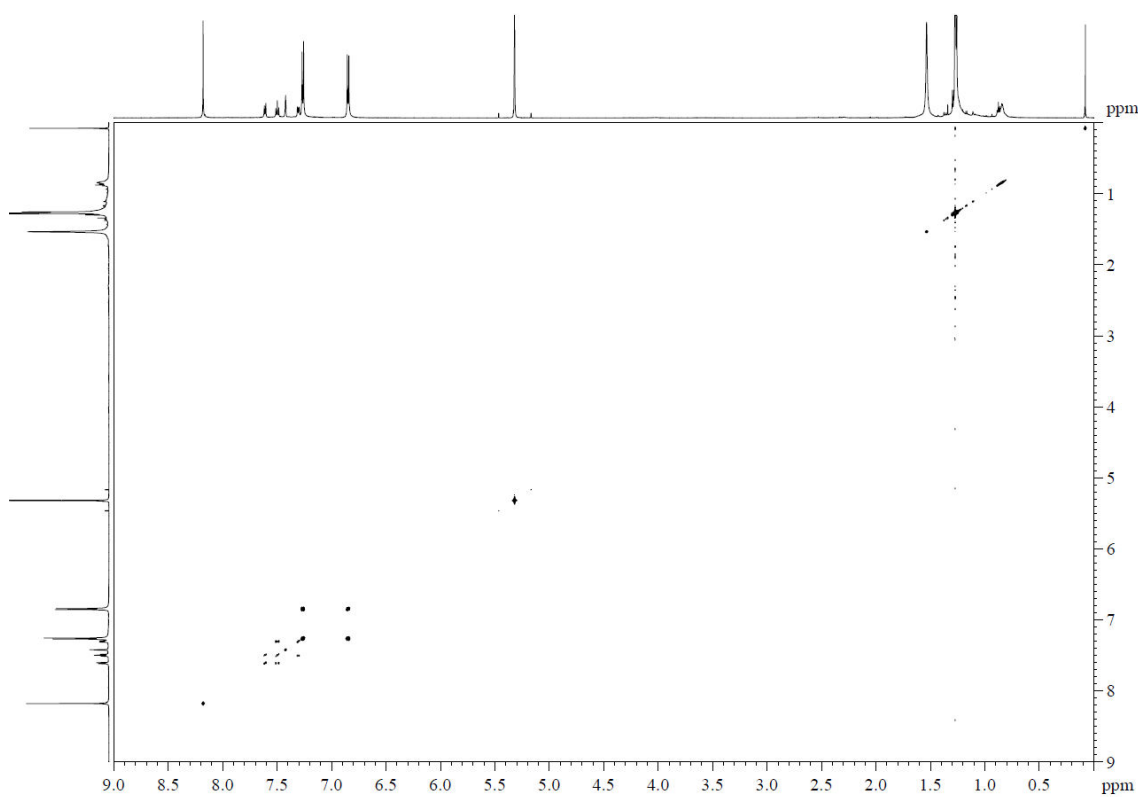


Fig. S19 (¹H, ¹H) COSY NMR spectrum of pentamer **3c**.

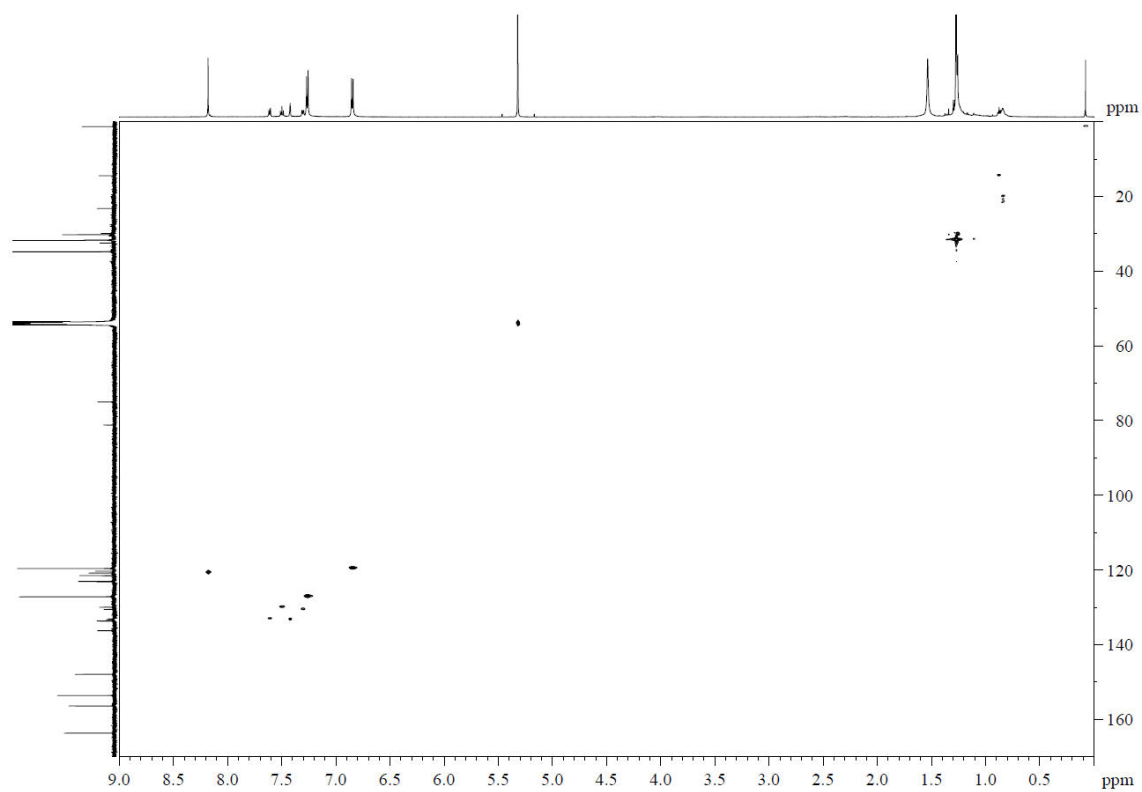


Fig. S20 (^1H , ^{13}C) HSQC NMR spectrum of pentamer **3c**.

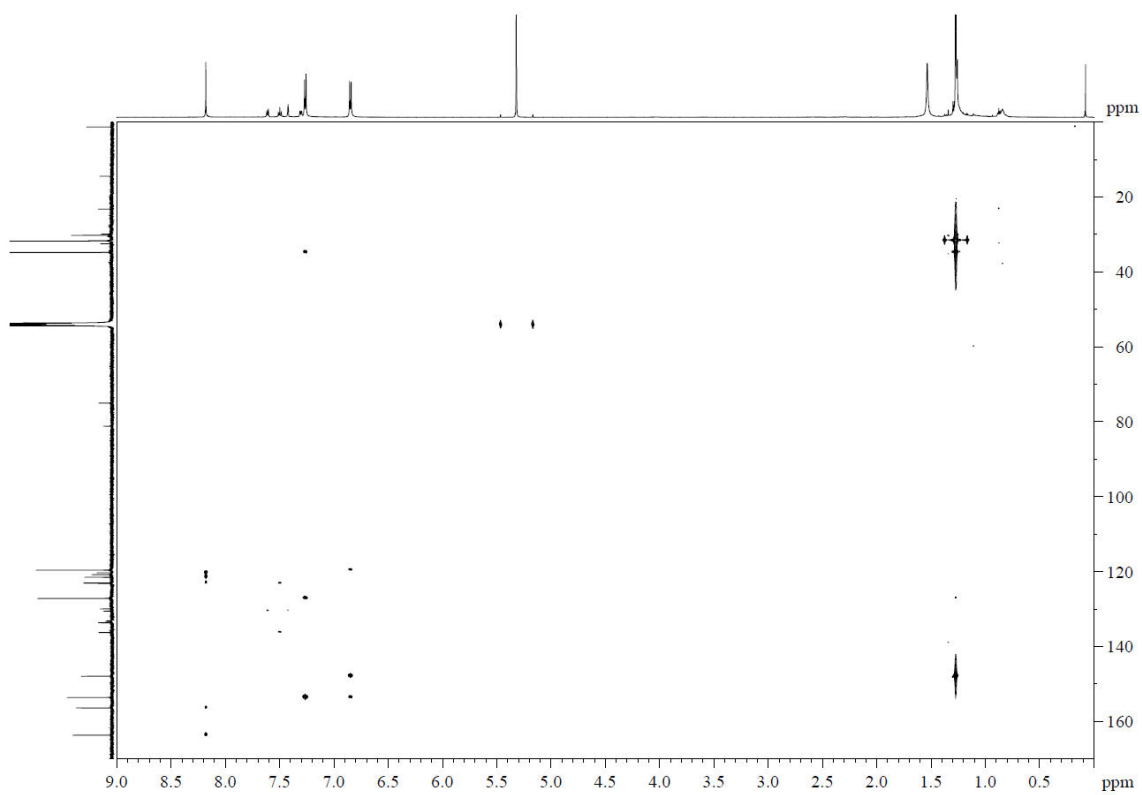


Fig. S21 (^1H , ^{13}C) HMBC NMR spectrum of pentamer **3c**.

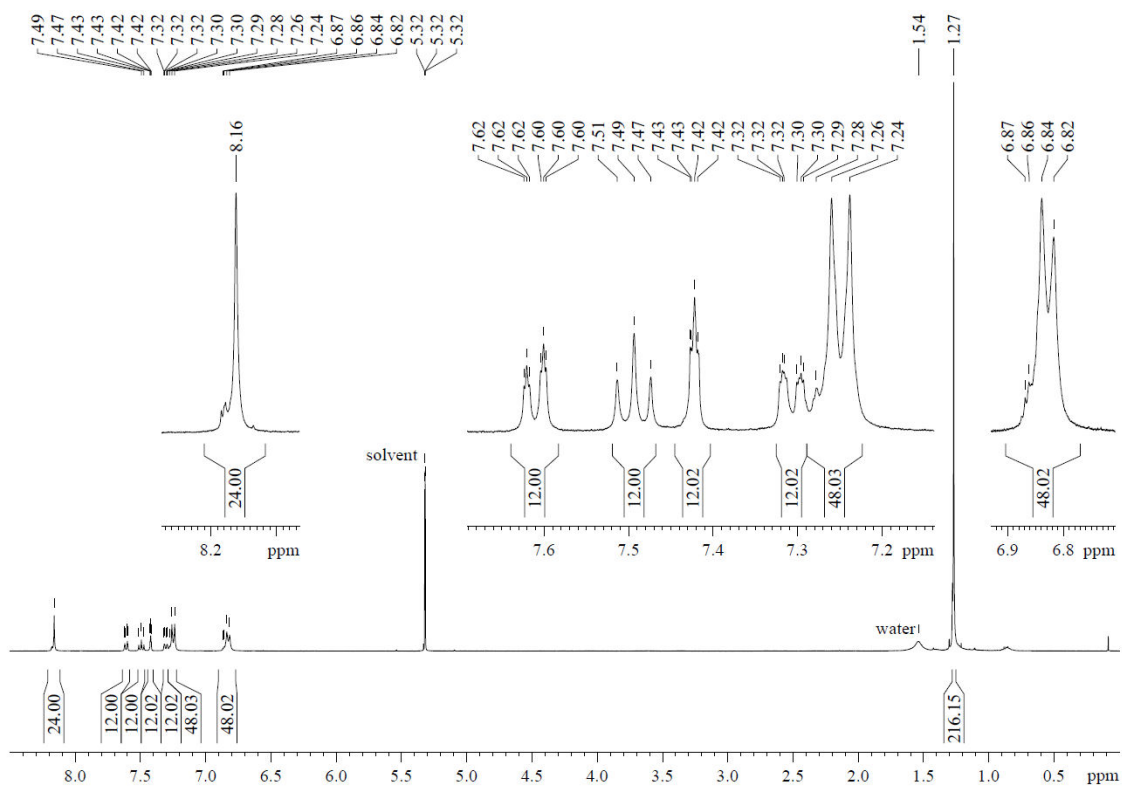


Fig. S22 ^1H NMR spectrum (600 MHz, CD_2Cl_2 , 298 K) of hexamer **3d**.

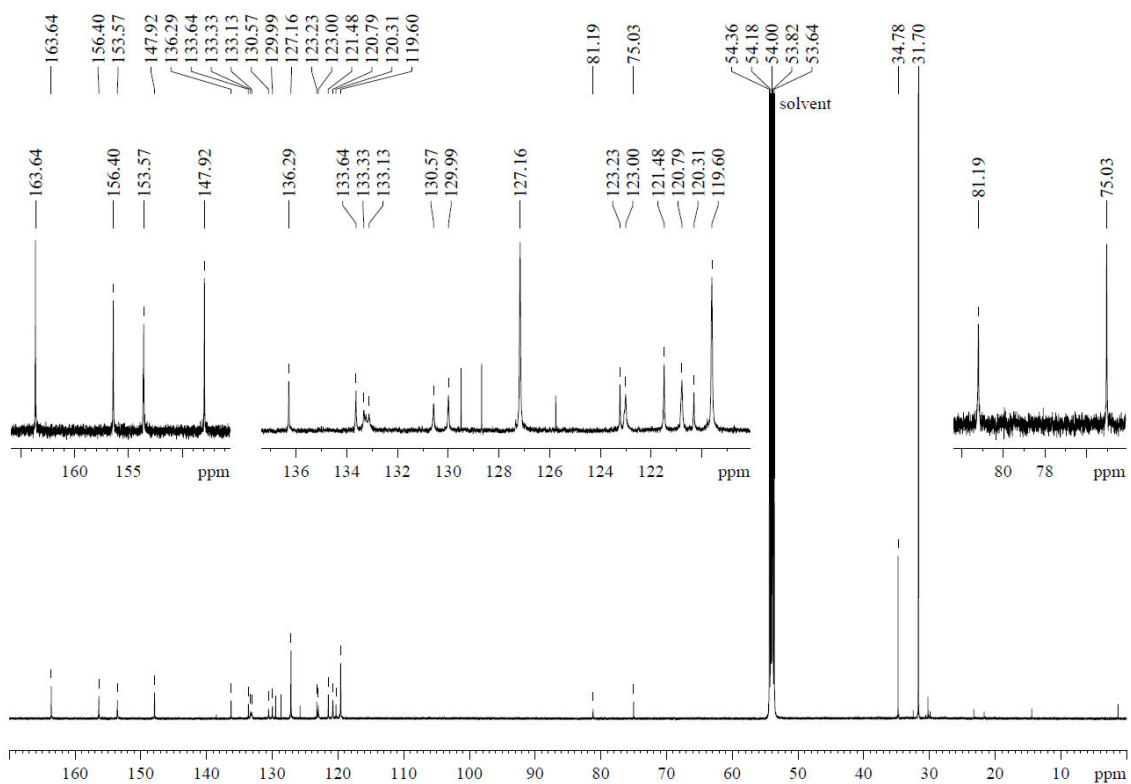


Fig. S23 ^{13}C NMR spectrum (150 MHz, CD_2Cl_2 , 298 K) of hexamer **3d**.

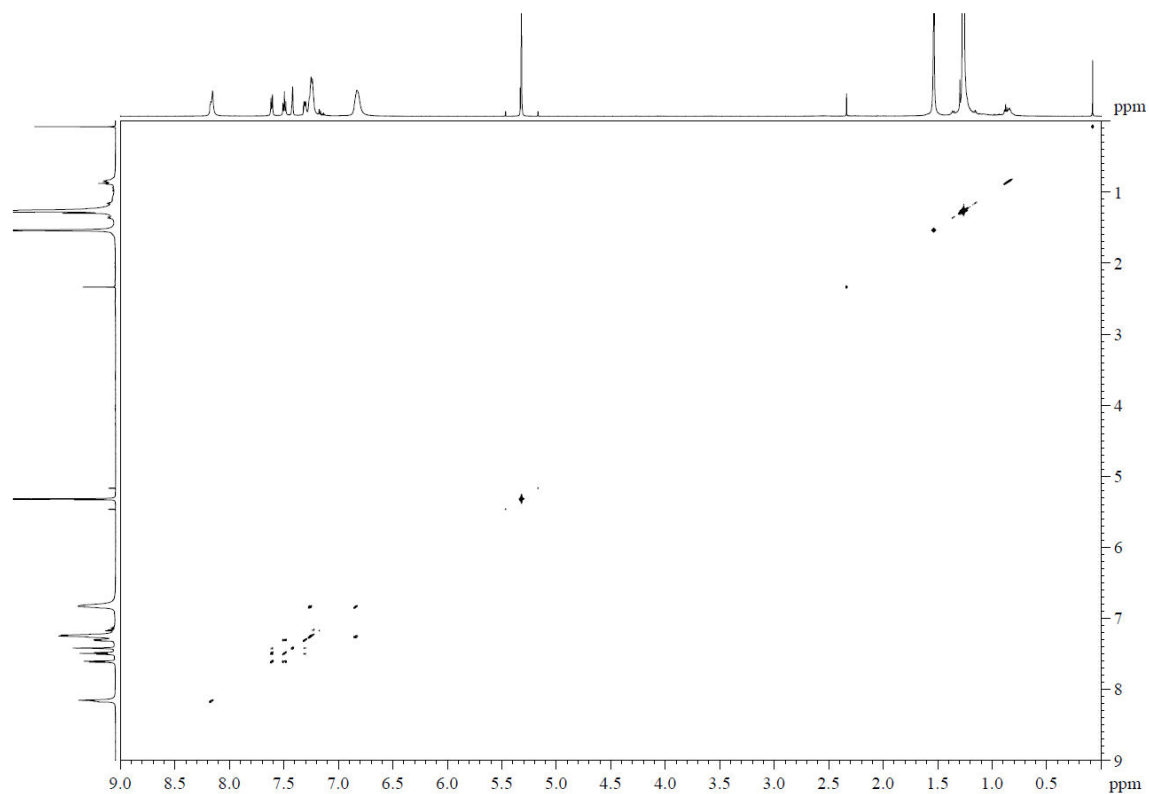


Fig. S24 (¹H,¹H) COSY NMR spectrum of hexamer **3d**.

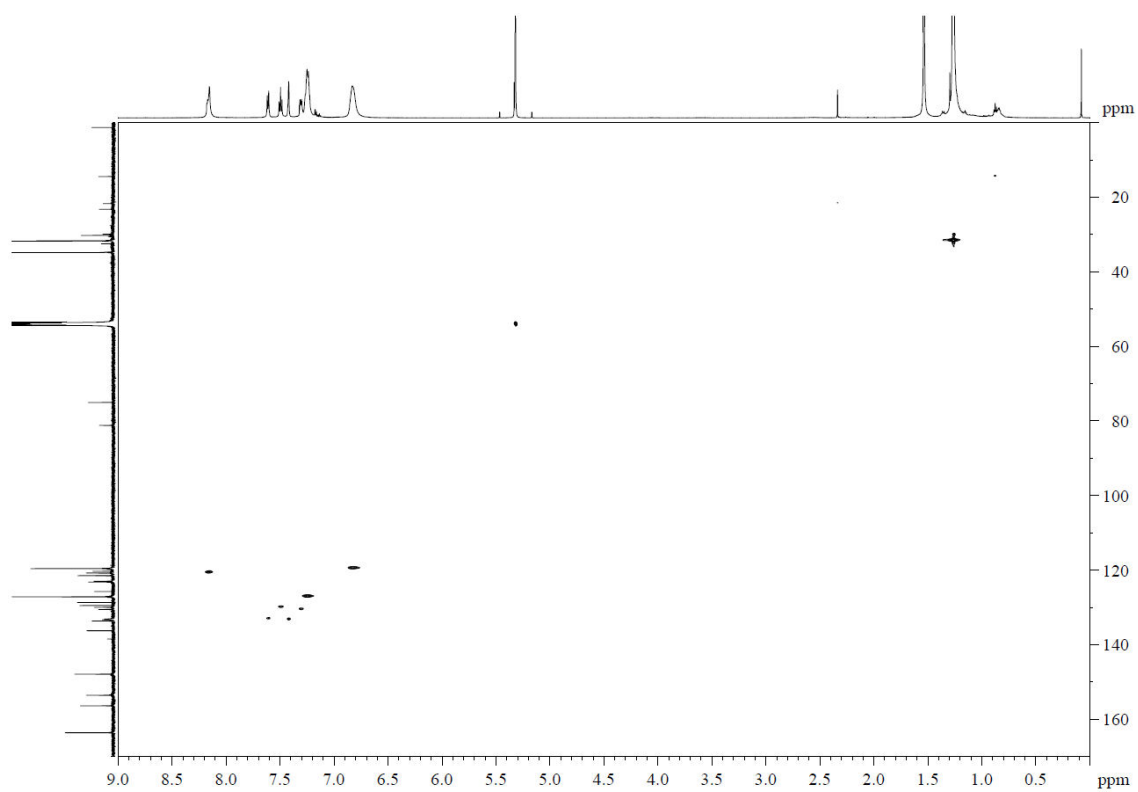


Fig. S25 (¹H,¹³C) HSQC NMR spectrum of hexamer **3d**.

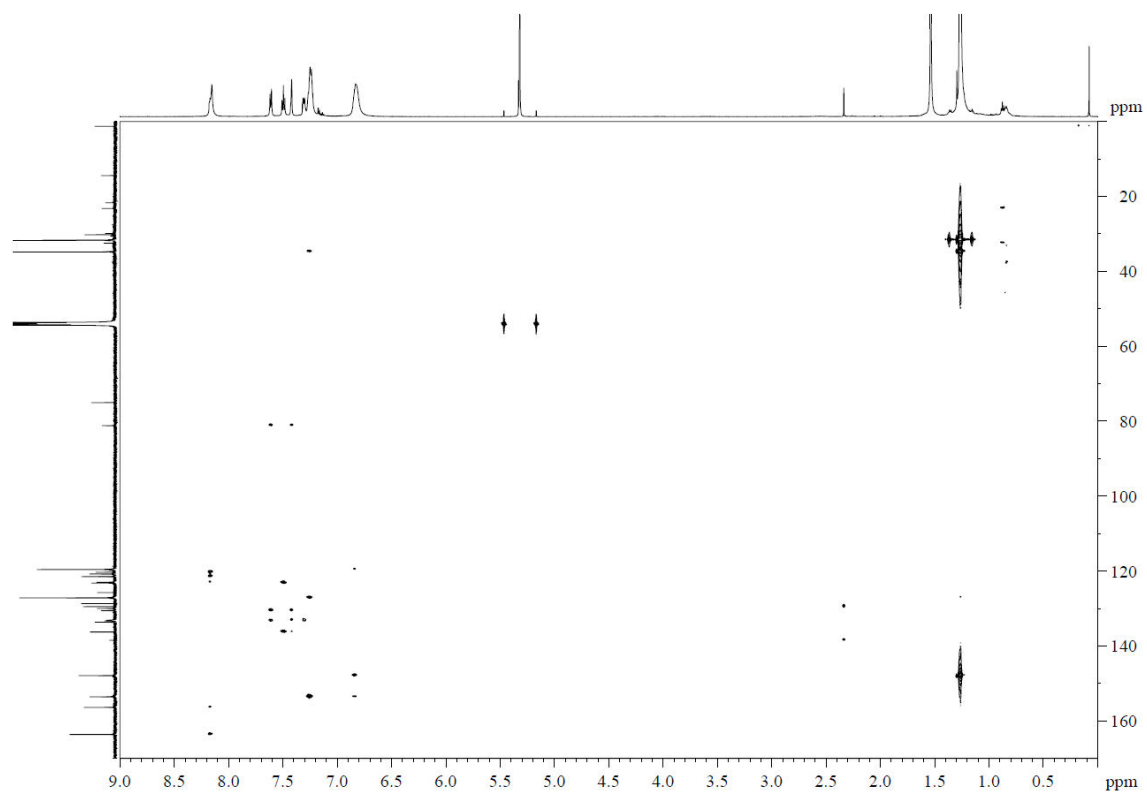


Fig. S26 (^1H , ^{13}C) HMBC NMR spectrum of hexamer **3d**.

5. High resolution mass spectra

Because the mass distribution $[M]^+$ is always overlaid by the double charged dimeric macrocycle $[2M]^{2+}$ itself, the mass distribution of the double charged monomeric macrocycle $[M]^{2+}$ is shown.

The top panel shows the calculated and the bottom one the measured mass distribution.

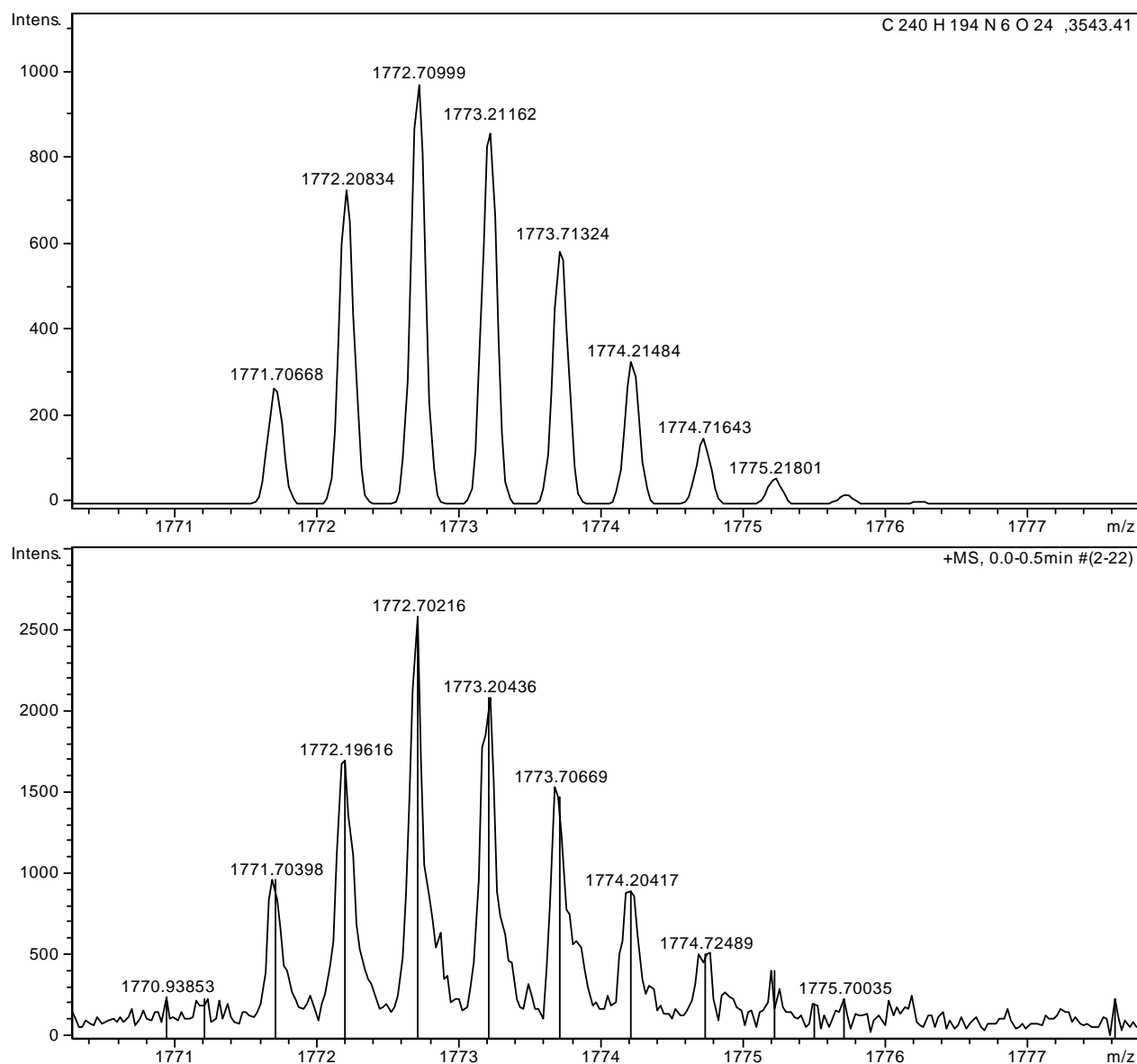


Fig. S27 Calculated (top) and measured (bottom) high resolution mass distribution (ESI) of trimer **3a**.

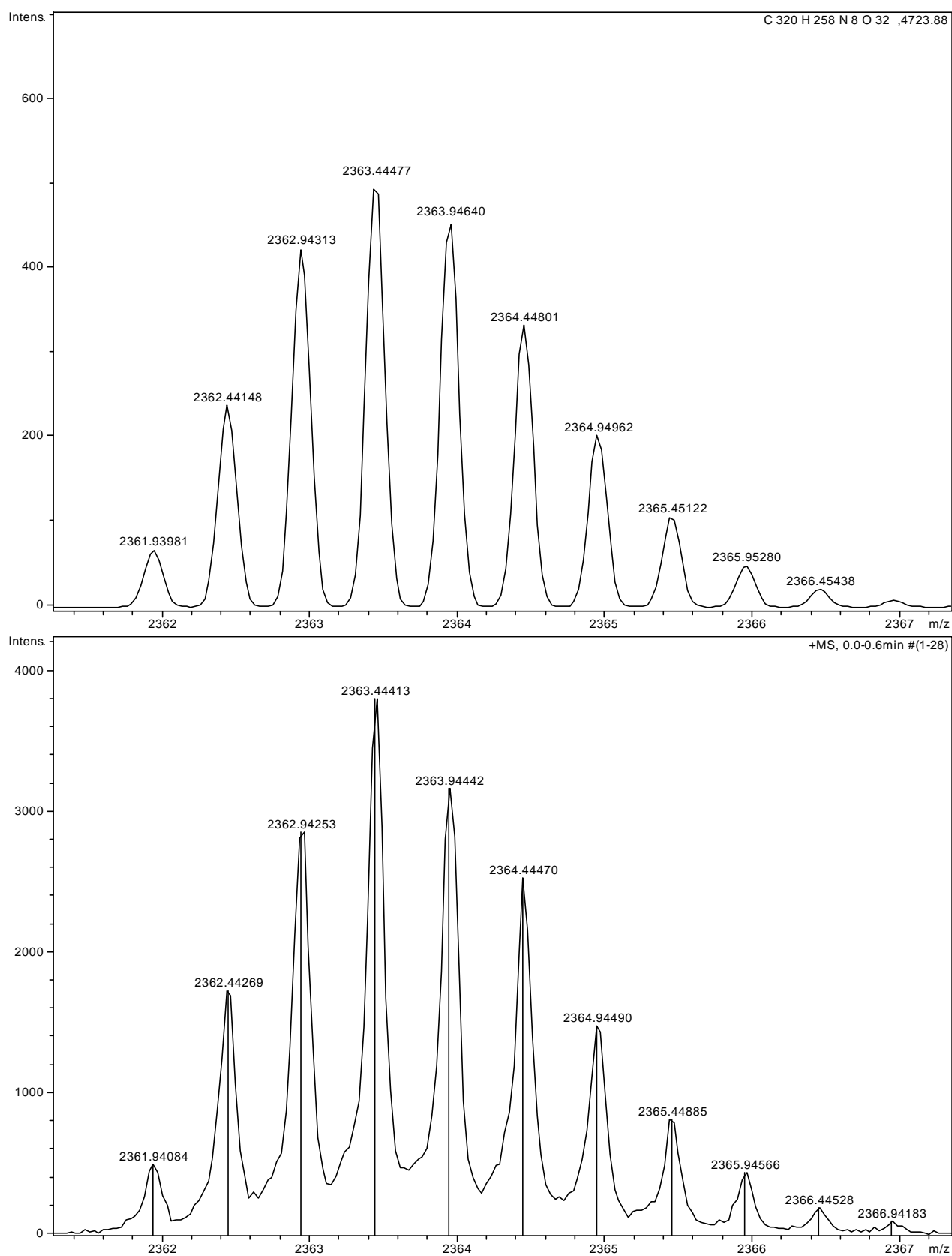


Fig. S28 Calculated (top) and measured (bottom) high resolution mass distribution (ESI) of tetramer **3b**.

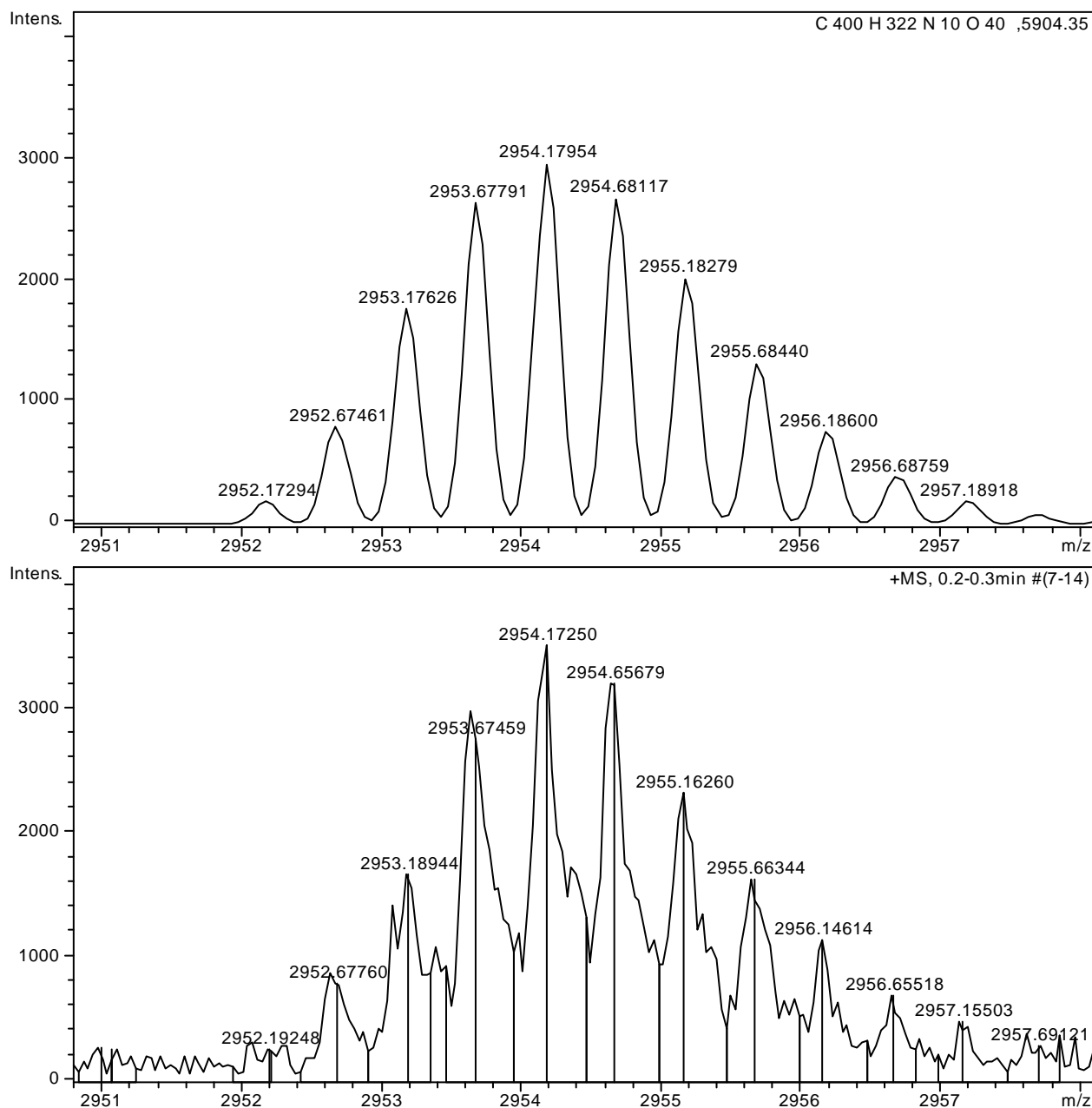


Fig. S29 Calculated (top) and measured (bottom) high resolution mass distribution (ESI) of pentamer **3c**.

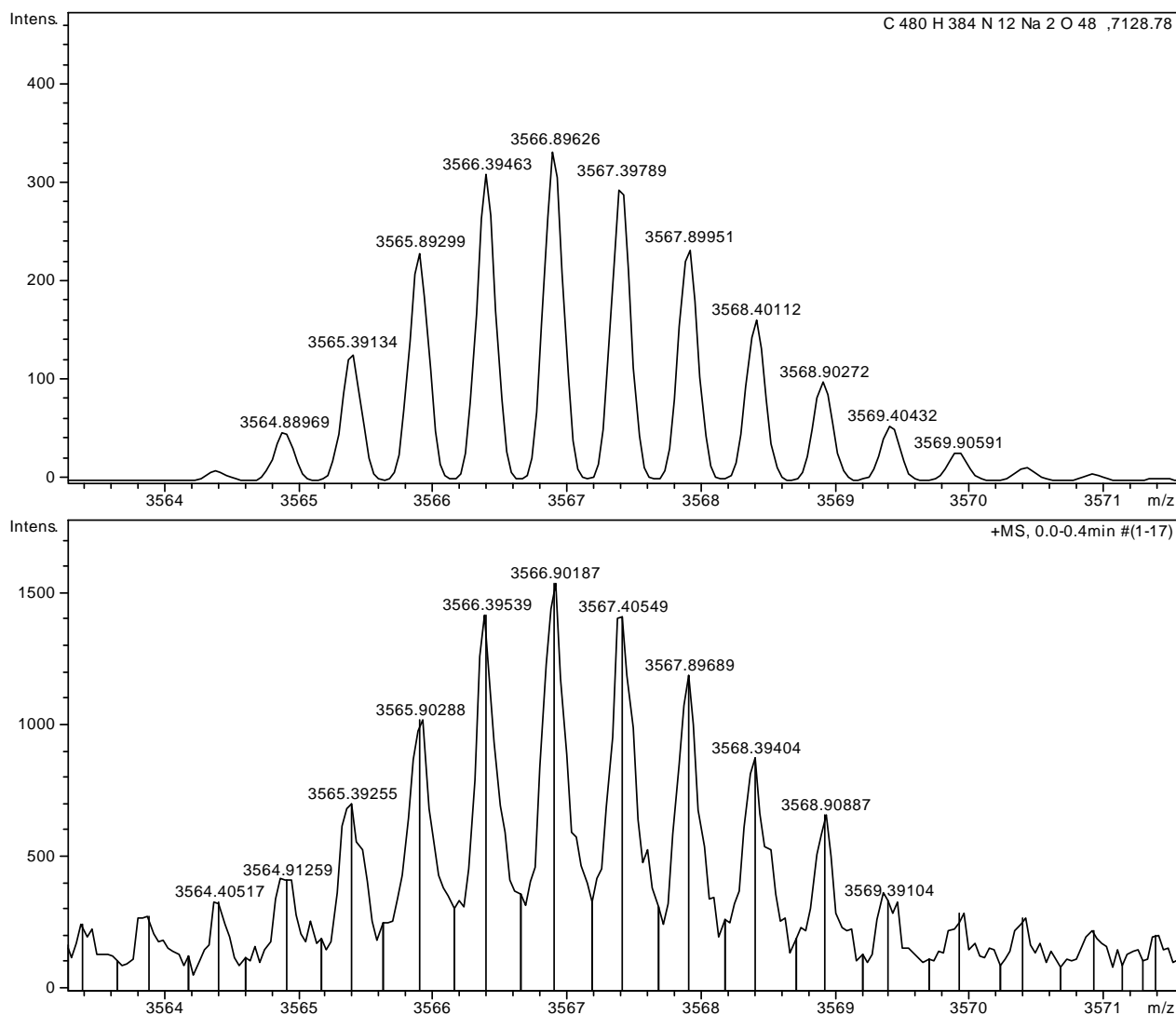


Fig. S30 Calculated (top) and measured (bottom) high resolution mass distribution (ESI) of hexamer **3d**.

6. Time-resolved fluorescence decay profiles

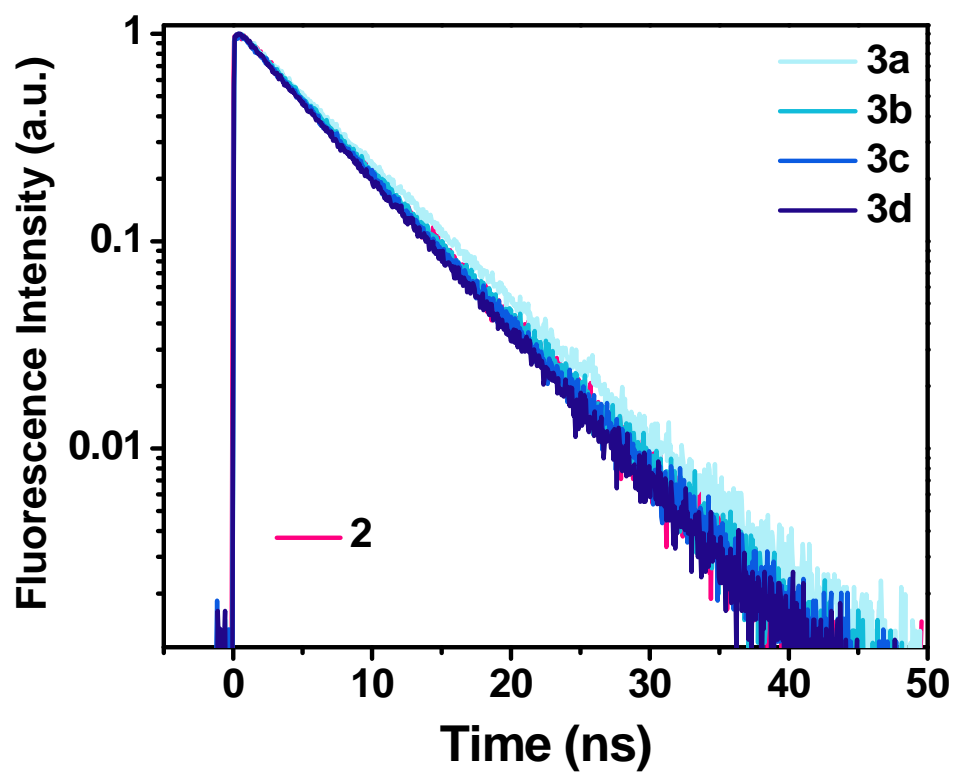


Fig. S31 Time-resolved fluorescence decay profiles of PBI monomer **2** and PBI macrocycles **3a-d** in CH_2Cl_2 by photoexcitation at 450 nm.

7. Transient absorption spectra and power-dependent transient absorption decay profiles

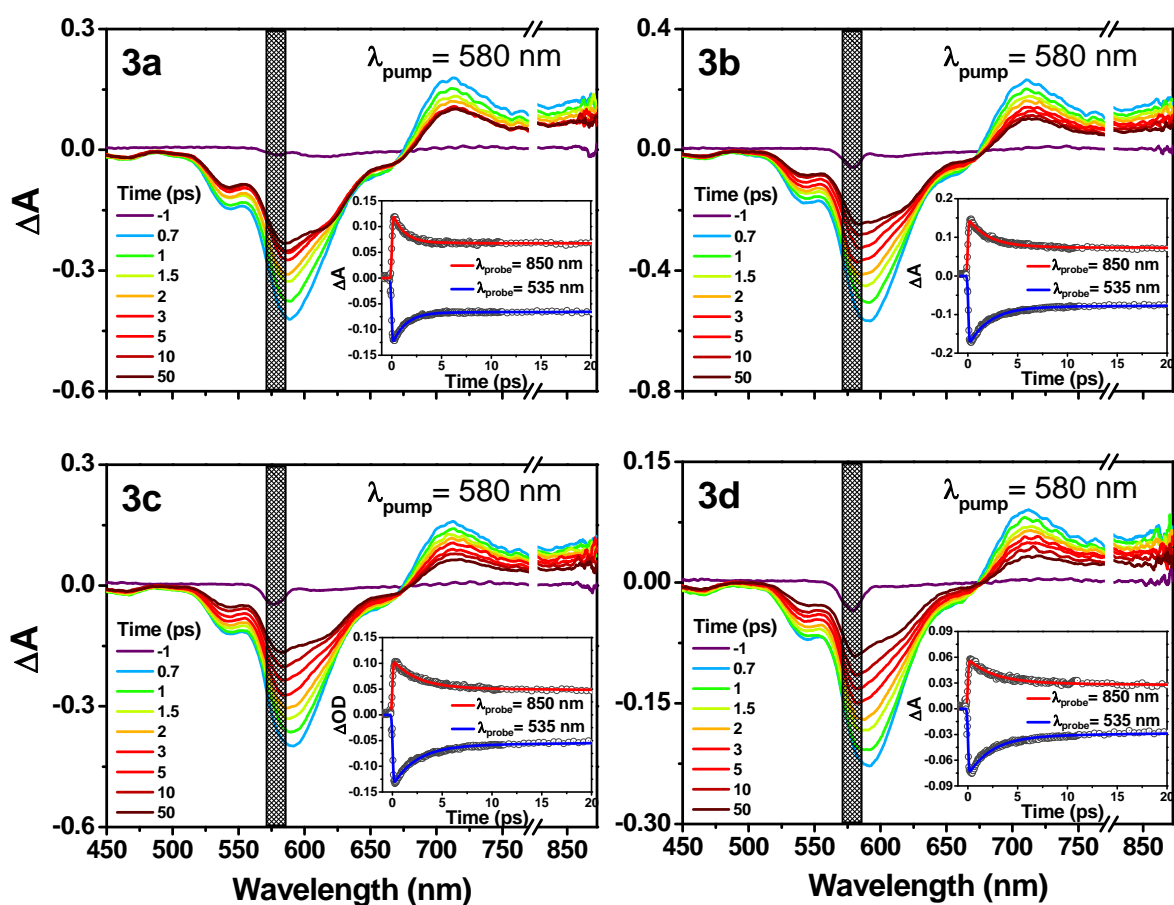


Fig. S32 Femtosecond transient absorption spectra of PBI macrocycles **3a-d** in CH_2Cl_2 . Insets show representative kinetic profiles of PBI macrocycles **3a-d**.

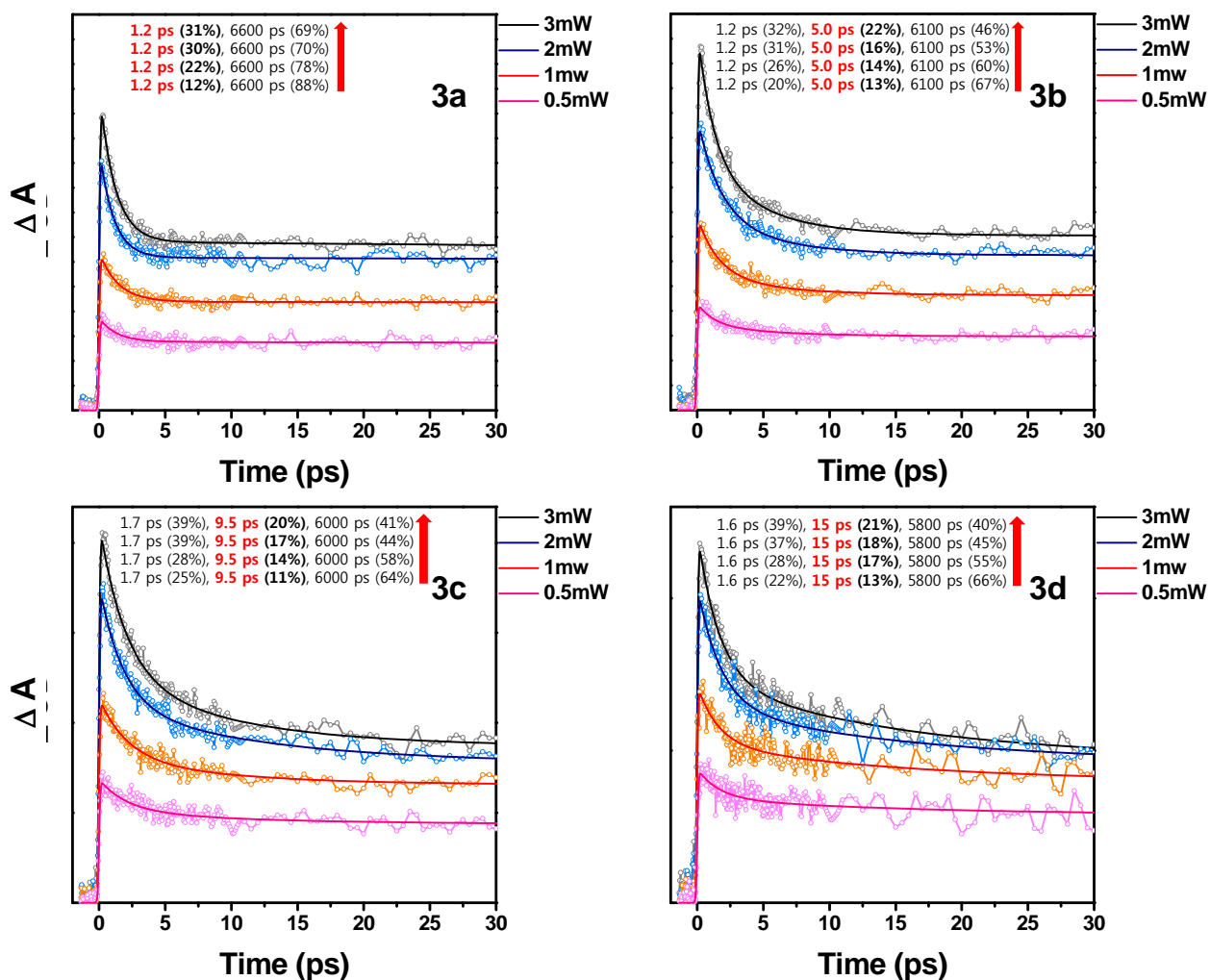


Fig. S33 Pump power-dependent transient absorption decay profiles of PBI macrocycles **3a-d** in CH_2Cl_2 , where pump and probe wavelengths were 580 and 850 nm, respectively.

8. References

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