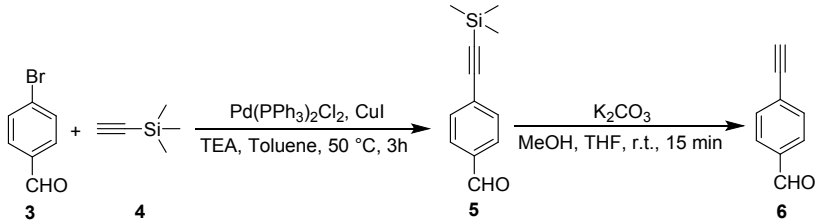
Supporting Information

Phenyleneethynylene trimer-based rigid-flexible [2+2] macrocycles for nucleic acid labelling in live cells

1. General Information

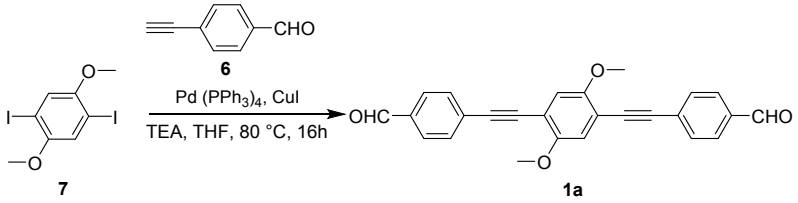
Chemicals, including solvents, were purchased from Fisher Scientific and used as received. Deuterated solvents were purchased from Cambridge Isotope Laboratories (Cambridge, MA). All chemicals and solvents were purchased and used without further purification. Nuclear magnetic resonance (NMR) spectra were recorded on a 400 MHz Avance Bruker NMR spectrometer. ^{1}H and ^{13}C NMR chemical shifts are given in ppm relative to $Si(CH_3)_4$. The mass spectrometric data were conducted on a Bruker Solarix FT-ICRMS. Data for crystal structure was obtained on a Bruker D8 Quest CMOS diffractometer. The crystal was kept at T = 296(2) K during data collection. Using APEX3, the structure was solved with the ShelXT 2014/5 structure solution program,[1] using the intrinsic phasing method. The model was refined with version 2016/6 of ShelXL[2] using full matrix least squares on F^2 minimization, using the Olex2 GUI.[3] Analytical thin layer chromatography (TLC) was performed on TLC Silica gel 60 F254. The TLC plates were visualized by shortwave (254 nm) or longwave (360 nm) UV light. Flash chromatography on silica gel (230–400 mesh) was performed. UV-vis spectra were recorded on a Varian Cary 50 Bio spectrophotometer. Fluorescence spectra were obtained using a FluoroLog-3 Spectrofluorometer (Jobin Yvon/Horiba). 9,10-diphenylanthracene (QY = 1.0) in cyclohexane was used as a fluorescence standard for QY determination. Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer Spectrum 100 FTIR Spectrometer. Fine polymer powders were directly mounted on an attenuated total reflection (ATR) cell of the spectrometer.

2. Synthesis of monomers

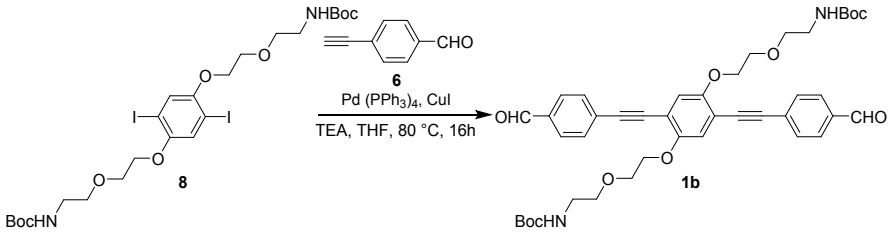


Synthesis of 4-ethynylbenzaldehyde (6) was conducted by following the literature procedure.[4]A solution of 4-bromobenzaldehyde (**3**) (5.0 g, 27.024 mmol) in dry toluene (70 mL) and triethylamine (35 mL) was degassed with nitrogen for 20 min. To this, trimethylsilyl acetylene (**4**) (2.8 g, 28.507 mmol) was added and the resulting mixture was degassed for additional 15 min. Pd $[PPh_3)]_4$ (947.2 mg, 1.351 mmol) and CuI (257.4 mg, 1.351 mmol) were added. The reaction mixture stirred at room temperature for 3h under nitrogen atmosphere. On completion, the organic solvent was evaporated to dryness. The residue was re-dissolved in dichloromethane and filtered through a silica gel column using mixture of ethyl acetate and hexane (1:9) to give compound **5** as brown solid. Yield: 3.7 g (68%). The compound **5** (3.7,

18.288 mmol) was dissolved in a mixture of tetrahydrofuran and methanol (50 mL, 1:1) and anhydrous potassium carbonate (2.5 g, 18.288 mmol) was added. The reaction mixture was allowed to stir at room temperature for 15 min, filtered and washed thoroughly with dichloromethane. The combine filtrate was evaporated and purified through column chromatography using mixture using mixture of ethyl acetate and hexane (2:8) to give compound **6** as yellow solid. Yield: 2.3 g (97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.02 (s, 2H), 7.84 (d, *J* = 8.4Hz, 2H), 7.63 (d, *J* = 8.4Hz, 2H), 3.29 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.4, 136.1, 132.8, 129.6, 128.4, 82.8, 81.2.



Synthesis of monomer 4,4'-((2,5-dimethoxy-1,4-phenylene)bis(ethyne-2,1-diyl))dibenzaldehyde (1a) was conducted by following the literature procedure.[5] Yield: 640 mg (63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.03 (s, 2H), 7.88 (d, *J* = 8.0Hz, 4H), 7.71 (d, *J* = 8.4Hz, 4H), 7.06 (s, 2H), 3.93 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.5, 154.3, 135.7, 132.4, 129.7, 129.6, 115.9, 113.6, 94.6, 89.8, 56.7.



Synthesis of di-tert-butyl (((((2,5-diiodo-1,4-phenylene)bis(oxy))bis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl))dicarbamate (8):
Monomers **8** was synthesized according to literature procedures.[6]

Synthesis of di-tert-butyl (((((2,5-bis((4-formylphenyl)ethynyl)-1,4-phenylene)bis(oxy))bis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl))dicarbamate (**1b**):
A solution of compounds **8** (1 g, 1.362 mmol) and **6** (390.0 mg, 2.997 mmol) in a mixed solution of dry tetrahydrofuran and triethylamine (28 mL, 3:1) was degassed with nitrogen for 20 min. $Pd(PPh_3)_4$ (47.7 mg, 0.068 mmol) and CuI (13.0 mg, 0.068 mmol) were added. The reaction mixture stirred at 80 °C for 16 h under nitrogen atmosphere. The mixture was allowed to cool down, filtered and the solvent was evaporated. The residue was purified by column chromatography using mixture of ethyl acetate and hexane (4:6) to give monomer **1b** as yellow solid. Yield: 480 mg (48%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.03 (s, 2H), 7.88 (d, *J* = 8.4Hz, 4H), 7.67 (d, *J* = 8.4Hz, 4H), 7.09 (s, 2H), 4.92 (br, 2H), 4.22 (t, *J* = 4.8Hz, 4H), 3.90 (t, *J* = 4.8Hz, 4H), 3.68 (t, *J* = 5.2Hz, 4H), 3.34-3.32 (m, 4H), 1.40 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ

191.5, 156.1, 153.9, 135.7, 132.2, 129.8, 129.5, 117.7, 114.4, 94.7, 89.6, 79.4, 70.8, 69.6, 40.6, 28.5. HR-ESI-FT-ICR-MS: m/z calculated for $C_{42}H_{48}N_2O_{10}$ $(M+H)^+$: 741.33817, found: 741.33812.

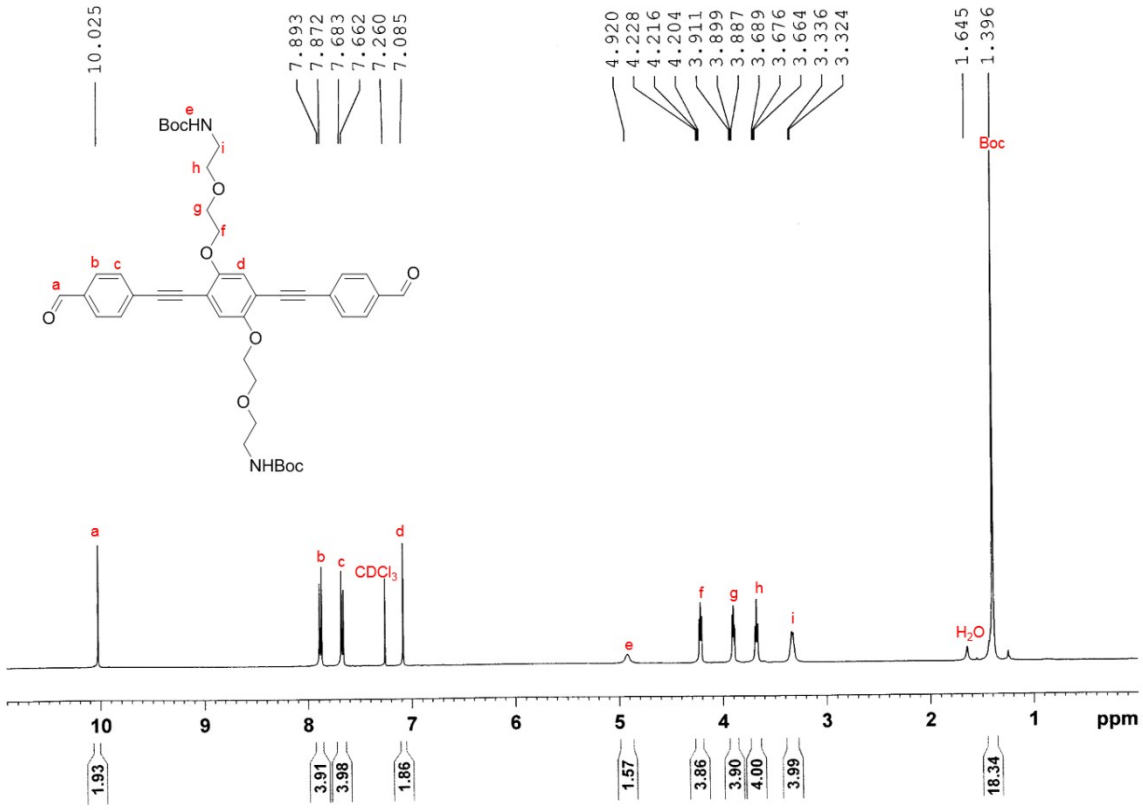


Figure S1. ^{1}H NMR spectrum of **1b** ($CDCl_3$).

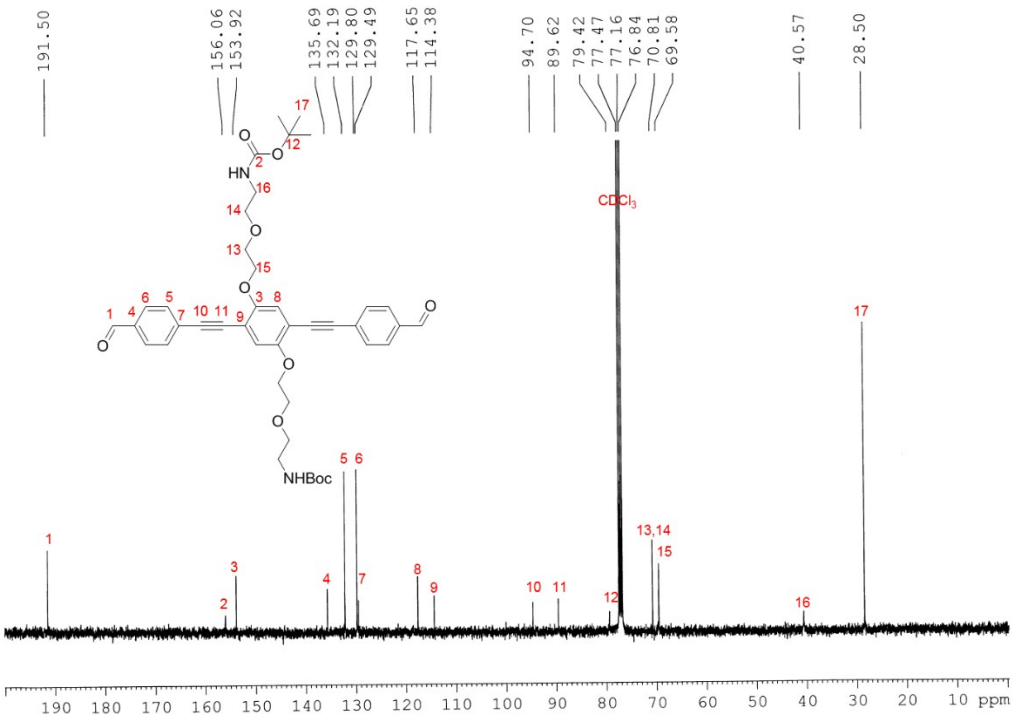
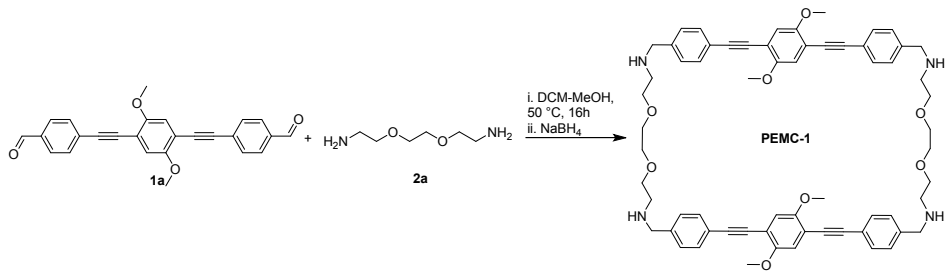


Figure S2. ^{13}C NMR spectrum of **1b** ($CDCl_3$).

3. Synthesis of PEMCs and PE trimer:

General procedure for macrocycle synthesis: To an oven dried round bottom flask, **1a** or **1b** (0.127 mmol) was dissolved in dichloromethane. To this solution, diamines (0.127 mmol) were added and the mixture was diluted with methanol. The reaction mixture was stirred at 50 °C for 10 h and allowed to cool down to room temperature. To the resulting reaction mixture, a solution of sodium borohydride (1.270 mmol) in methanol (5 mL) was added dropwise at 20 °C. The reaction mixture was stirred at room temperature for 1 h and then excess sodium borohydride was quenched by adding saturated aqueous sodium bicarbonate solution (1 mL). The solvent was evaporated, and then the residue was re-dissolved in dichloromethane (50 mL). The solution was washed with aqueous ammonium chloride solution (15%), water, and brine. The organic layer was separated, dried over anhydrous sodium sulfate, filtered, and evaporated. The crude macrocycles were purified by column chromatography or recrystallization from acetonitrile.

Synthesis of PEMC-1:



Prepared from **1a** (50.1 mg, 0.127 mmol) and **2a** (18.8 mg, 0.127 mmol) in a mixture of dichloromethane (20 mL) and methanol (40 mL) over 10 h by following the general procedure. Recrystallization from acetonitrile yielded **PEMC-1** as off-white crystals. Yield: 48.7 mg (75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, J = 8.4Hz, 8H), 7.27 (d, J = 8.4Hz, 8H), 6.92 (s, 4H), 3.83 (s, 12H), 3.77 (s, 8H), 3.62-3.60 (m, 16H), 3.77 (t, J = 4.8Hz, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.9, 140.8, 131.9, 128.2, 122.0, 115.7, 113.5, 95.1, 85.8, 70.6, 70.5, 56.5, 53.8, 48.9; HR-ESI-FT-ICR-MS: m/z calculated for $C_{64}H_{68}N_4O_8$ $(M+H)^+$: 1021.51099, found: 1021.51117.

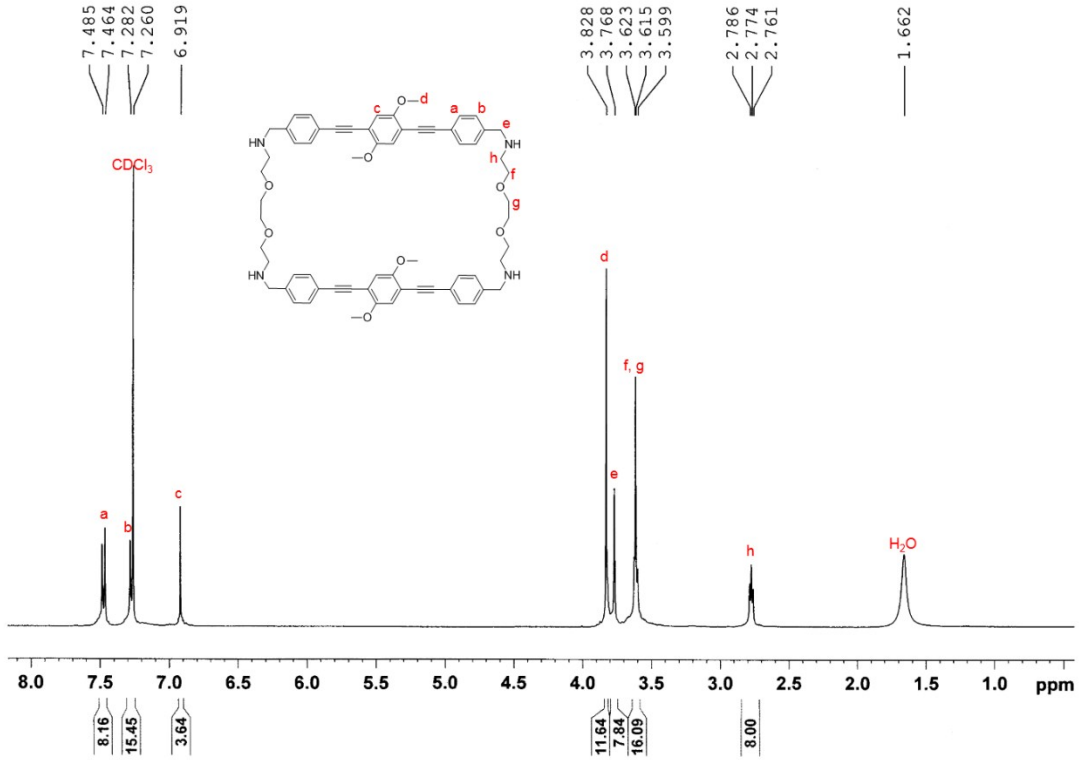


Figure S3. ^{1}H NMR spectrum of **PEMC-1** ($CDCl_3$).

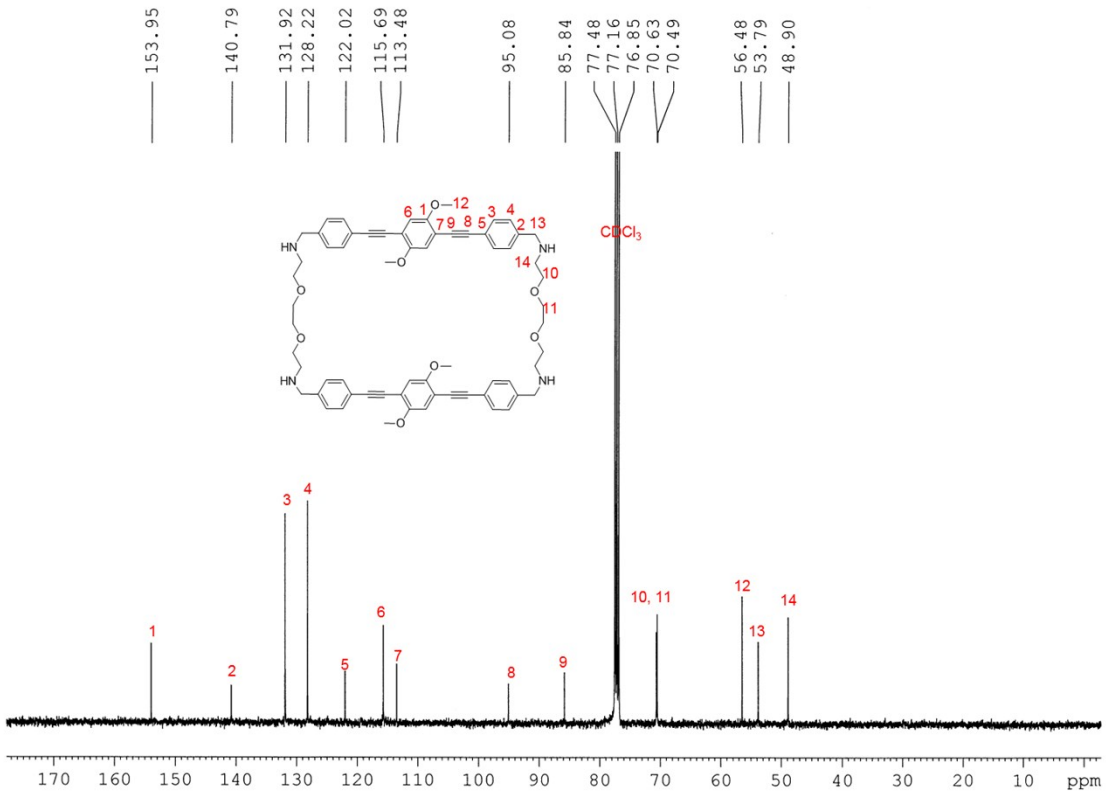
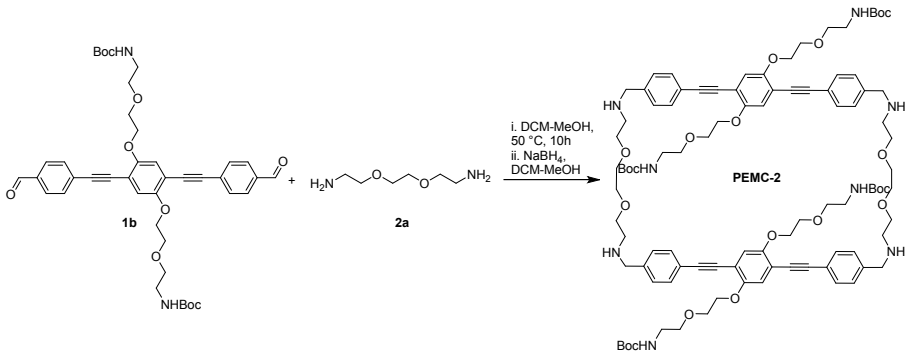


Figure S4. ^{13}C NMR spectrum of **PEMC-1** ($CDCl_3$).

Synthesis of PEMC-2:



PEMC-2 was prepared by reacting **1b** (94.1 mg, 0.127 mmol) and **2a** (18.8 mg, 0.127 mmol) in a mixed solvent of dichloromethane (40 mL) and methanol (80 mL) over 10 h by following the general procedure. Purified by silica gel column chromatography using mixture of dichloromethane, methanol, and aq. ammonia as an eluent yielded **PEMC-2** as off white solid. Yield: 99 mg (91%). ^1H NMR (400 MHz, CDCl3): δ 7.40 (d, J = 8.4Hz, 8H), 7.26 (d, J = 8.4Hz, 8H), 6.89 (s, 4H), 5.10 (br, 4H), 4.08 (t, J = 4.4Hz, 8H), 3.77-3.75 (m, 16H), 3.63-3.59 (m, 24H), 3.27-3.25 (m, 8H), 2.78 (t, J = 4.8Hz, 8H), 1.39 (s, 36H); ^{13}C NMR (100 MHz, CDCl3): δ 156.2, 153.6, 140.5, 131.8, 128.4, 122.0, 117.5, 114.3, 95.3, 85.8, 79.2, 70.8, 70.4, 70.3, 69.6, 69.5, 53.6, 48.8, 40.6, 28.6; HR-ESI-FT-ICR-MS: m/z calculated for $C_{96}H_{128}N_8O_{20}$ $(M+H)^+$: 1713.93176, found: 1713.93180.

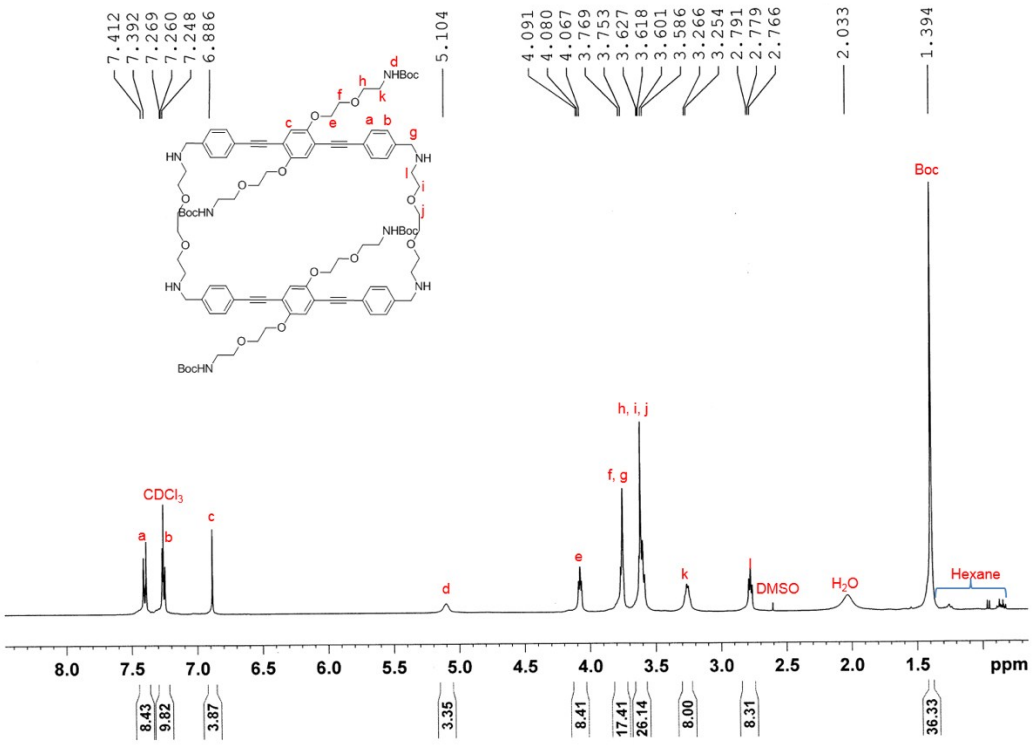


Figure S5. ^{1}H NMR spectrum of **PEMC-2** ($CDCl_3$).

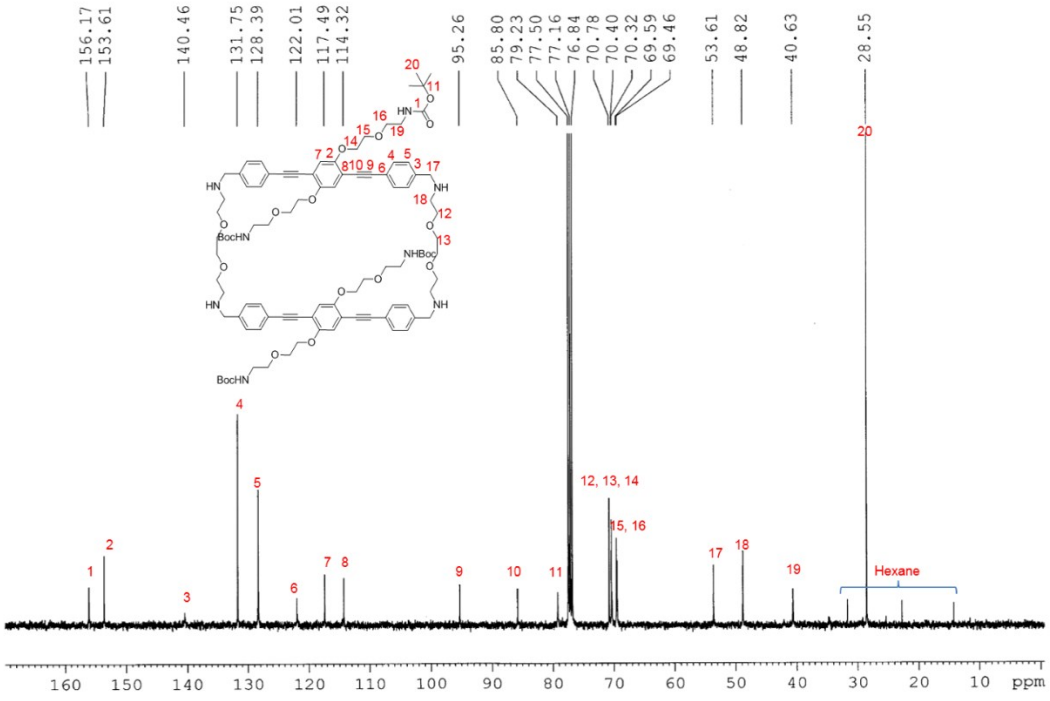
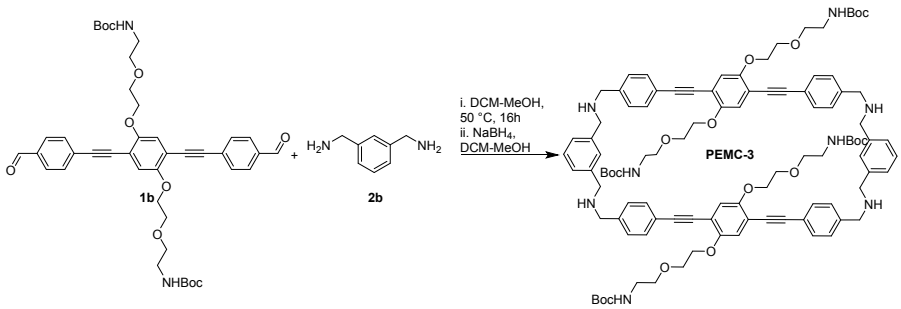


Figure S6. ^{13}C NMR spectrum of **PEMC-2** ($CDCl_3$).

Synthesis of PEMC-3:



PEMC-3 was prepared by reacting **1b** (94.1 mg, 0.127 mmol) and **2c** (68.1 mg, 0.127 mmol) in a mixture of dichloromethane (40 mL) and methanol (80 mL) over 10 h by following the general procedure. Recrystallization from acetonitrile yielded **PEMC-3** as off white solid. Yield: 87 mg (81%). ^{1}H NMR (400 MHz, CDCl3): δ 7.47 (d, *J* = 8.0Hz, 8H), 7.41 (br, 2H), 7.33 (d, *J* = 8.0Hz, 8H), 7.30 (s, 2H), 7.25 (br, 2H), 6.94 (s, 4H), 5.00 (br, 4H), 4.06 (t, *J* = 4.4Hz, 8H), 3.84-3.78 (m, 24H), 3.60 (t, *J* = 5.2Hz, 8H), 3.24-3.23 (m, 8H), 1.38 (s, 36H); ^{13}C NMR (100 MHz, CDCl3): δ 156.1, 153.7, 153.4, 140.7, 140.1, 131.8, 128.7, 127.7, 127.2, 122.1, 117.6, 114.4, 95.3, 85.7, 79.3, 70.8, 69.6, 52.6, 52.4, 40.6, 28.5. HR-ESI-FT-ICR-MS: m/z calculated for $C_{100}H_{120}N_8O_{16}$ $(M+H)^+$: 1689.88951, found: 1689.88834.

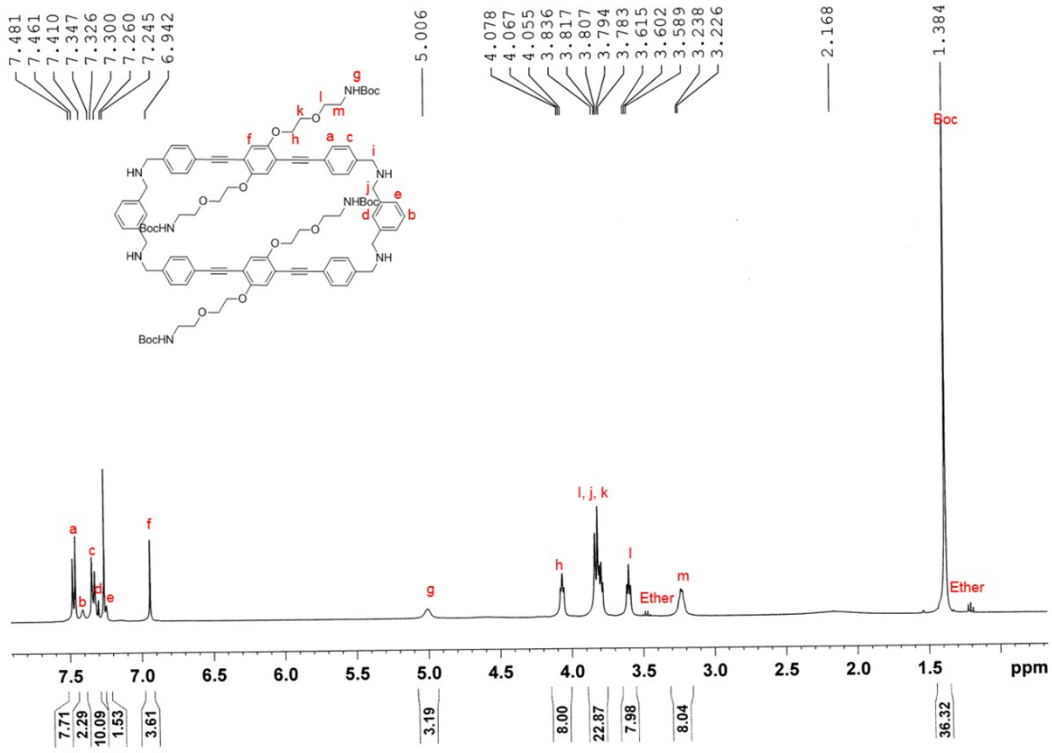


Figure S7. ^{1}H NMR spectrum of **PEMC-3** ($CDCl_3$).

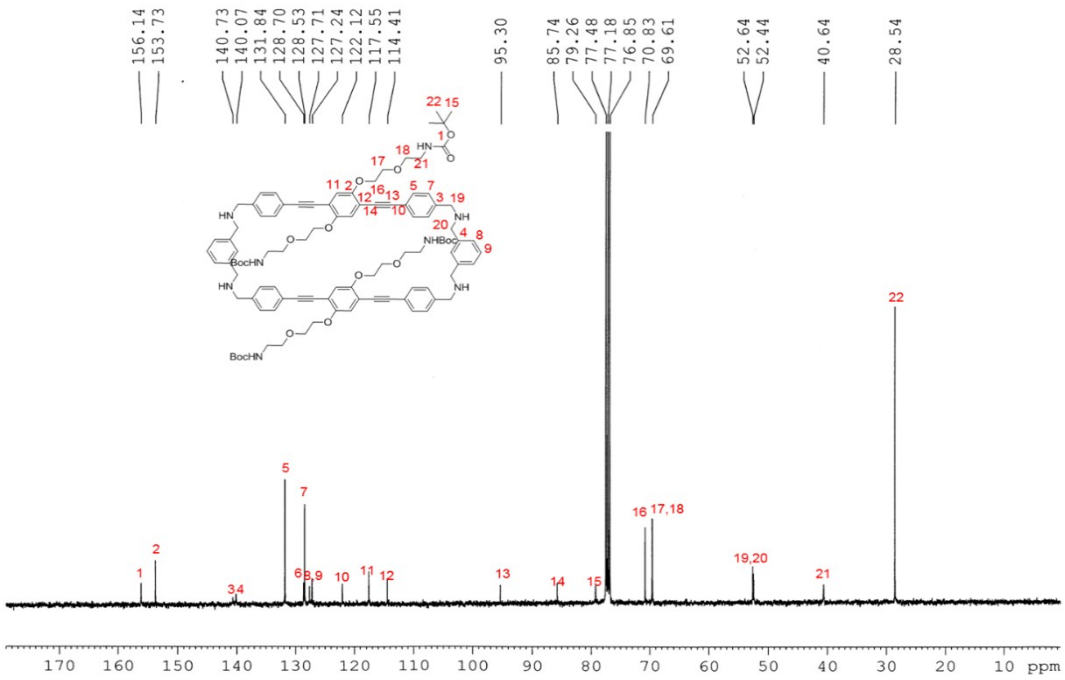


Figure S8. ^{13}C NMR spectrum of **PEMC-3** ($CDCl_3$).

Synthesis of PE trimer control:

Compound 1b (135 mg, 0.18 mmol) was dissolved in 5 mL of MeOH. 2-(2-Aminoethoxy)ethanol (48 mg, 0.47 mmol) was added to the solution followed by stirring at 50 ℃ for 24 h. The mixture was cooled down to room temperature and $NaBH_4$ (34 mg, 0.91 mmol) was added to the mixture. After 12 h, solvent was evaporated, and the crude product was re-dissolved in 10ml of DCM. The solution was extracted with a dilute NaOH solution (20 mL x2). The organic fraction was purified by preparative TLC (1:1 EA/MeOH). The product was pale yellow powder. Yield: 21mg (13%). ^1H NMR (600 MHz, Chloroform): δ 7.47-7.48 (d, 4H), 7.30-7.31 (d, 4H), 7.03 (s, 2H), 4.99 (s, 0.8H), 4.17-4.19 (t, 4H), 3.68-3.87 (t, 4H), 3.81 (s, 4H), 3.70-3.72 (t, 4H), 3.66-3.68 (t, 4H), 3.62-3.63 (t, 4H), 3.57-3.58 (t, 4H), 3.29-3.30 (t, 4H), 2.80-2.82 (t, 4H), 1.39 (s, 18H). ^{13}C NMR (500 MHz, Chloroform): δ 156.14, 153.75, 140.60, 131.77, 128.38, 122.00, 117.77, 114.51, 95.30, 85.60, 79.30, 72.44, 70.82, 70.40, 69.71, 69.65, 61.94, 53.67, 48.79, 40.61, 28.50. HRMS (ESI): Calculated for $C_{50}H_{70}N_4O_{12}$ $[M+H]^+$: 919.50630; found $[M+H]^+$: 919.50726.

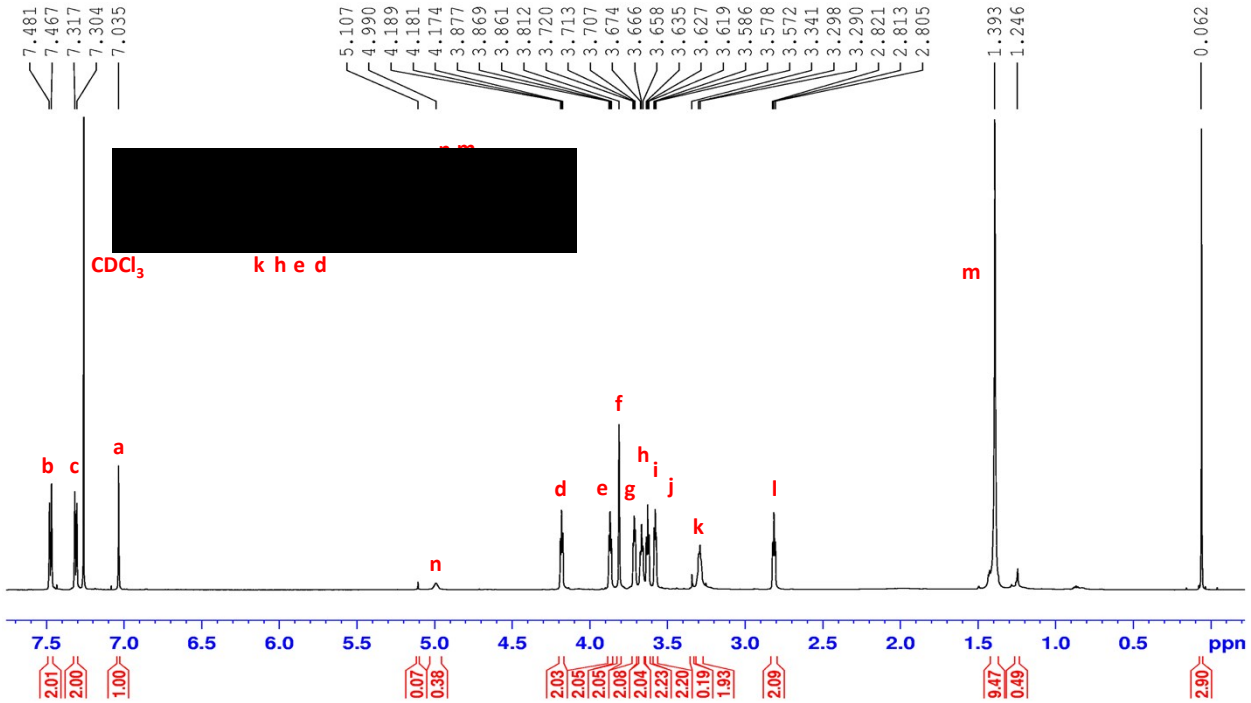


Figure S9. [1]H NMR spectrum of **PE trimer control**.

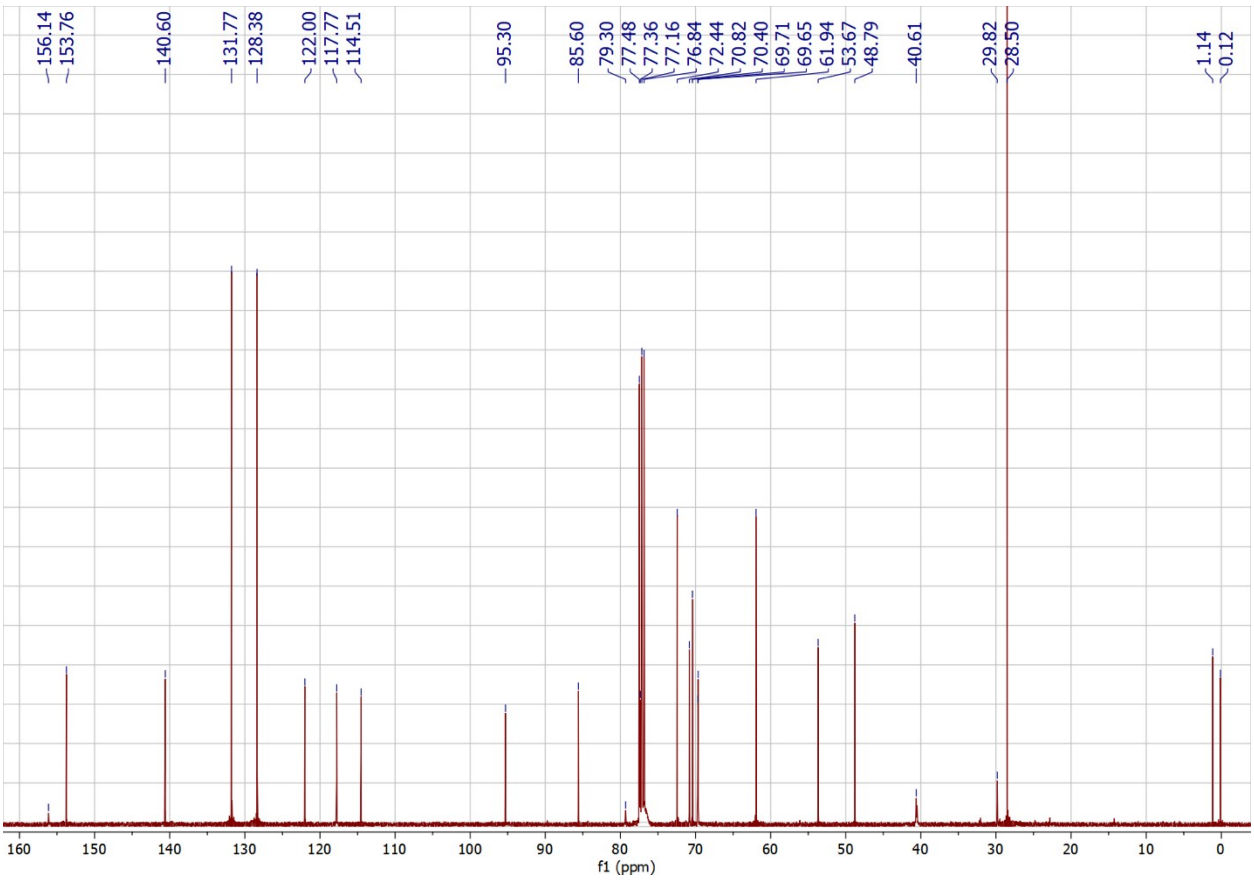
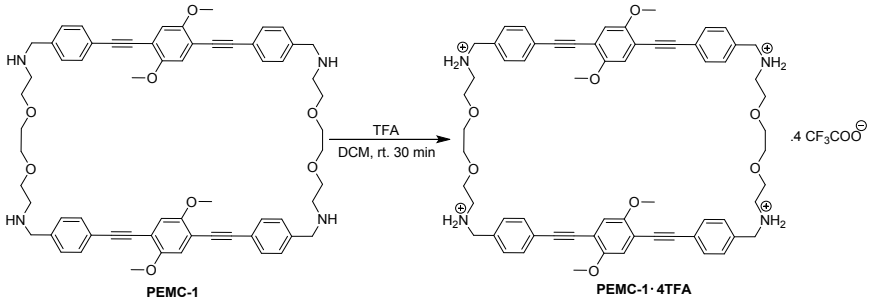


Figure S10. [13]C NMR spectrum of **PE trimer control**.

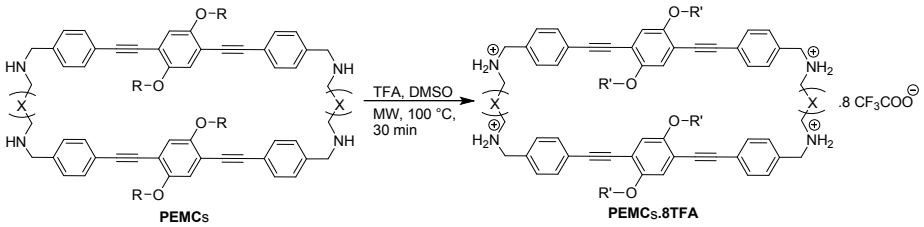
4. Protonation and deprotection of macrocycles

Synthesis of PEMC-1·4TFA:



To a solution of **PEMC-1** (15 mg, 0.015 mmol) in dichloromethane (1 mL), trifluoroacetic acid (0.5 mL) was added. The reaction mixture was allowed to stir at room temperature for 30 min. The organics were evaporated, and the residue was precipitated from diethylether and dried in *vacuo* to give compound **PEMC-1·4TFA** as off-white solid. Yield: 16 mg (100%).^{1}H NMR (400 MHz, MeOD-d_4): δ 9.14 (br, 8H), 7.51 (d, J = 8.0Hz, 8H), 7.46 (d, J = 8.0Hz, 8H), 7.00 (s, 4H), 4.18 (s, 8H), 3.80 (s, 12H), 3.70 (t, J = 4.8Hz, 8H), 3.62 (s, 8H), 3.08 (m, 8H).

Synthesis of PEMC-2·8TFA to PEMC-4·8TFA:



General procedure for Boc-deprotection:

To a solution of **PEMCs** in DMSO (0.5 mL), trifluoroacetic acid (0.1 mL) was added. The mixture was heated at 100 °C in a microwave for 30 min. After cooling, the resulting reaction mixture was dropwise added to diethyl ether and stirred until precipitate was formed. The precipitates were collected and dried in *vacuo* to give compound **PEMCs·8TFA** as off-white solid in quantitative yield.

Synthesis of PEMC-2·8TFA: Yield: 21 mg (quantitative). ^{1}H NMR (400 MHz, MeOD-d_4): δ 7.49 (d, J = 8.4Hz, 8H), 7.45 (d, J = 8.4Hz, 8H), 6.94 (s, 4H), 4.24 (s, 8H), 4.16 (t, J = 4.0Hz, 8H), 3.90 (t, J = 4.4Hz, 8H), 3.88-3.79 (m, 16H), 3.71 (s, 8H), 3.26 (t, J = 4.8Hz, 8H), 3.06 (t, J = 5.2Hz, 8H).

Synthesis of PEMC-3·8TFA: Yield: 39 mg (99%).^{1}H NMR (400 MHz, D_2O): δ 7.60 (m, 6H), 7.40 (d, J = 7.6Hz, 8H), 7.33 (d, J = 7.6Hz, 8H), 7.08 (s, 2H), 7.04 (s, 4H), 4.31-4.39 (m, 16H), 4.14 (s, 8H), 3.97 (br, 8H), 3.86 (t, J = 4.8Hz, 8H), 3.18 (t, J = 4.4Hz, 8H).

Synthesis of PE trimer control·4TFA: Yield: 72%. ^{1}H NMR (400 MHz, Methanol): δ 7.60-7.63 (d, 4H), 7.55-7.57 (d, 4H), 7.2 (s, 2H), 4.29 (s, 4H), 4.26-4.28 (t, 4H), 3.96-3.98 (t, 4H), 3.85-3.87 (t, 4H), 3.76-3.79 (t, 4H), 3.71-3.73 (t, 4H), 3.6-3.62 (t, 4H), 3.29-3.31 (m, 4H).

5. Photophysical Properties of PEMCs and PE trimer

Table S1. Photophysical properties of PEMCs and PE trimer in water

Compounds	ε ($M^{-1}cm^{-1}$)	QY[a] (%)	$\lambda_{max,ab}$ (water)	$\lambda_{max,em}$ (water)
PEMC-1·4TFA	40000	3.8	306, 373	458
PEMC-2·8TFA	32400	2.4	307, 355	456
PEMC-3·8TFA	33200	2.5	310, 358	440
PE trimer·4TFA	47000	0.9	306, 354	407

[a]9,10-Diphenylanthracene (QY = 1.0) in cyclohexane was used as a fluorescence standard for QY determination.

6. DNA and RNA complexation with PEMCs and PE-Trimer

UltraPure DNA solution from Calf Thymus and RNA from Escherichia Coli were purchased from Sigma Aldrich and used as received. The concentrations of both DNA and RNA solutions were determined by measuring the absorbance (the extinction coefficients of DNA and RNA are 6600 $cm^{-1}M^{-1}$ and 9250 $cm^{-1}M^{-1}$, respectively. Both concentrated DNA and RNA solutions were further diluted with RNase free water to obtain an 800 µM stock solution. 1 mM of each PEMC and PE trimer solution was further diluted with RNase free water to obtain 200 µM stock solutions. 10 µL of the PEMCs (or PE trimer) stock solution was mixed with 160 µL of the DNA (or RNA) stock solution followed by the addition of 230 µL of RNase free water. After gentle pipetting, absorbance and emission spectra were recorded at the excitation wavelength at 350 nm.

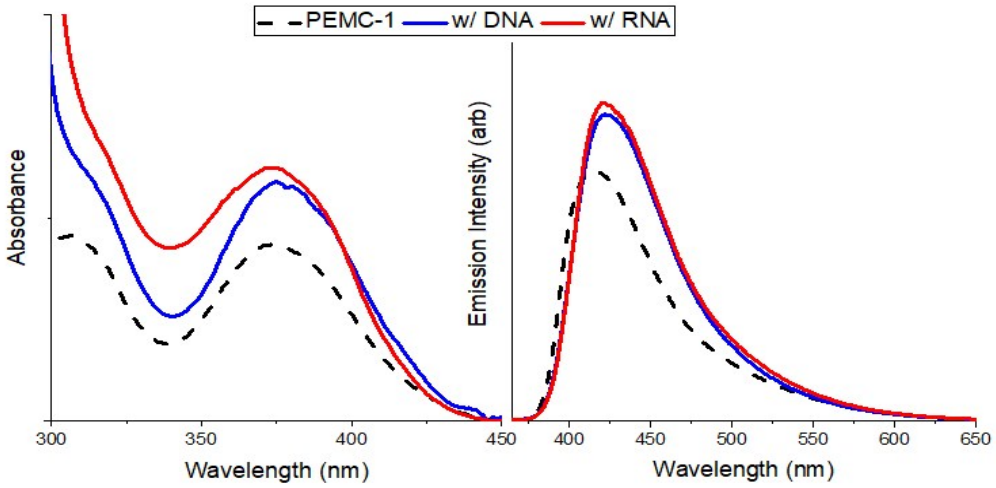


Figure S11. UV and Fluorescence spectra of PEMC-1 before (dotted) and after complexation with DNA (solid blue line) and RNA (solid red line). The concentrations of PEMC and NA were 5 µM and 320 µM, respectively.

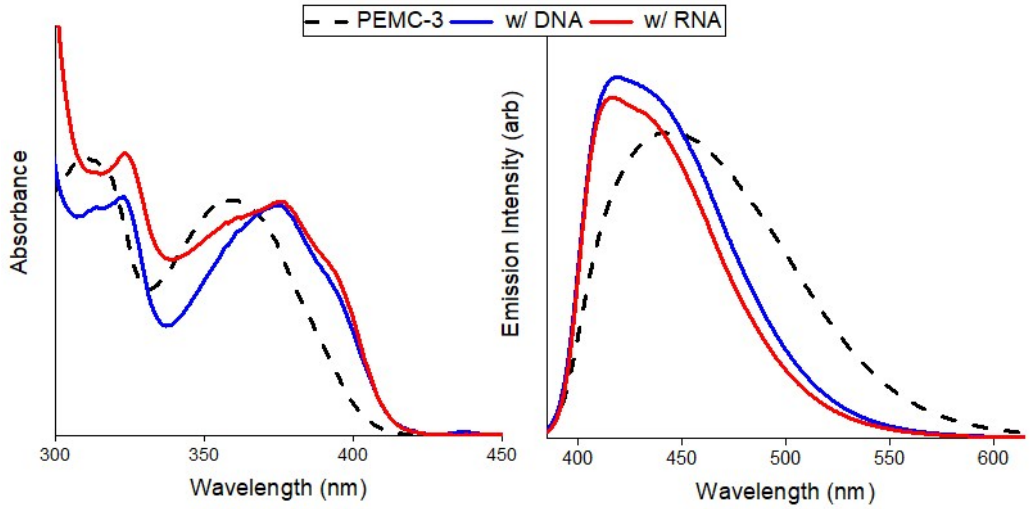


Figure S12. UV and Fluorescence spectra of PEMC-3 before (dotted) and after complexation with DNA (solid blue line) and RNA (solid red line). The concentrations of PEMC and NA were 5 μM and 320 μM, respectively.

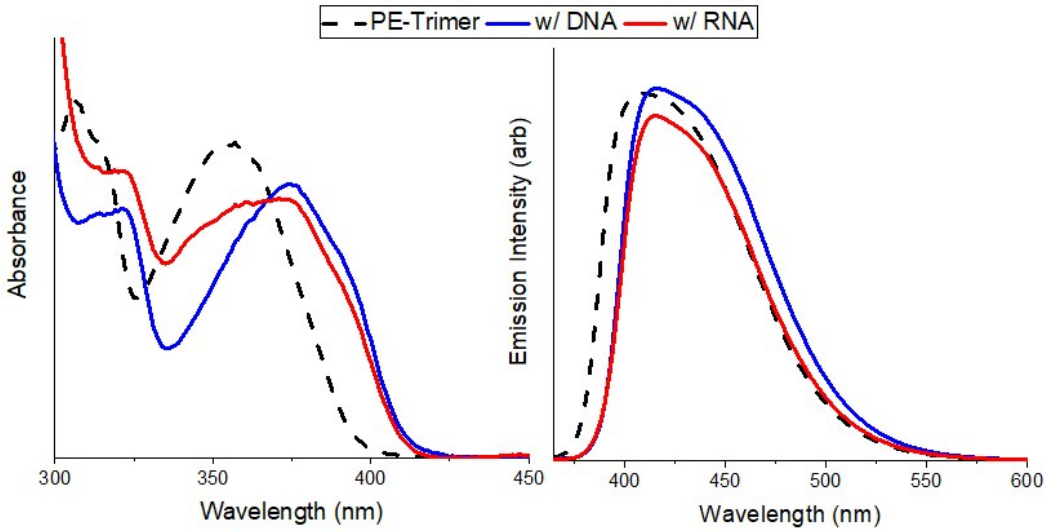


Figure S13. UV and Fluorescence spectra of PE trimer before (dotted) and after complexation with DNA (solid blue line) and RNA (solid red line). The concentrations of PEMC and NA were 5 μM and 320 μM, respectively.

7. Cellular toxicity study:

HeLa cells were seeded in a 96-well plate were seeded into a 96-well plate (~10,000 cells per well in 200 μL of a complete medium) and allowed to attach for one day at 37 °C under a humidified atmosphere of 5% CO_2. A stock solution of PEMC-1, PEMC-2, and PE trimer were added into a complete media and diluted to the required concentrations. Final concentrations of 40 μM, 20 μM,

10 μM, 5 μM, and 1 μM of PEMCs and PE trimer were added into the complete media by dilution with PEMCs and PE-Trimer stock solutions. After addition of PEMCs and PE trimer, the cells were incubated for additional 18 h. Cells were treated with 10 μL of methylthiazole tetrazolium (MTT) (5 mg/mL in PBS, CALBIOCHEM, Germany) and incubated for 4 h at 37 °C. 200 μL of medium was removed gently by using pipette and biological grade DMSO (100 μL) was added to solubilize the purple formazan crystals formed by proliferating cells. Absorbance was measured by a microplate well reader (infinite M1000 PRO, TECAN, Switzerland) at 570 nm. Relative cell viability (%) as a function of PEMCs and PE-Trimer concentration was expressed as percentage relative to the untreated control cells. All measurements were performed in triplicate and standard deviation was included in the error bar.

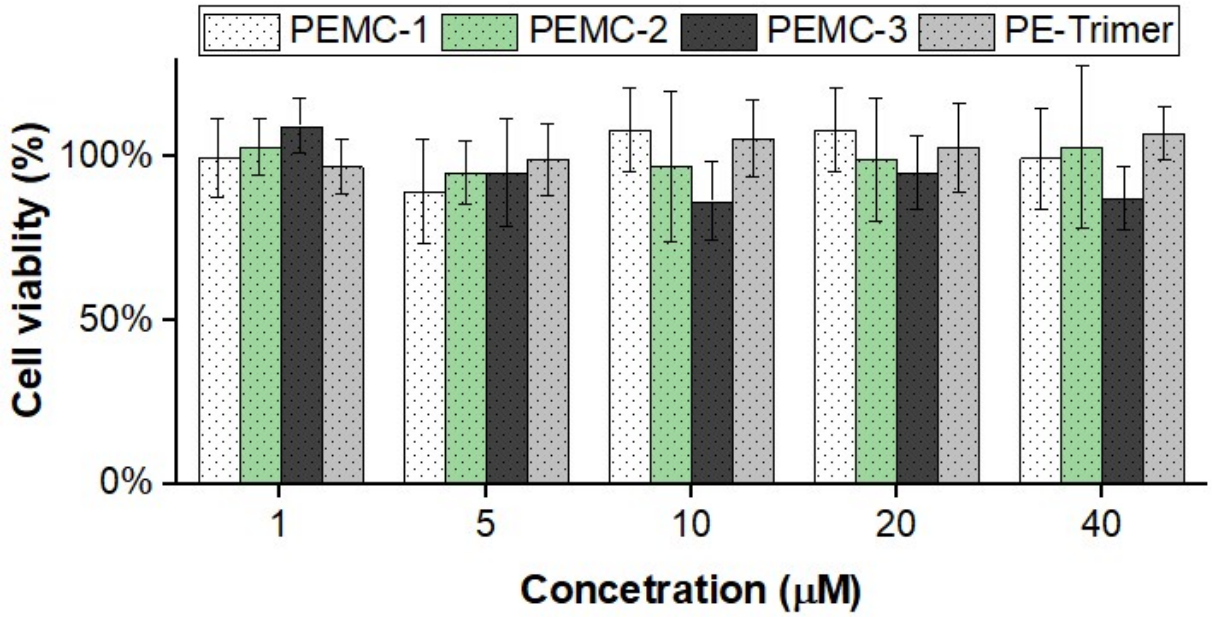


Figure S14. Cell viability inhibition of PEMC-1, PEMC-2, PEMC-3, and PE trimer.

8. Cell uptake studies by fluorescent microscopy:

HeLa cells were seeded into a 12-well plate (~20,000/well) containing glass coverslips one day before the PEMCs and PE trimer treatment. After incubation in a complete media for 24 h under 5% CO_2 at 37 °C, the medium was removed, and the cells were washed three times with PBS. PEMCs and PE trimer in a fresh complete medium, respectively, was added to cells (final concentration of 10 μM). After 1 h incubation, cells were washed three times with PBS followed by fixation with 4% PFA for 10 min. Fixed cells were then washed three times with PBS and the coverslips were mounted on microscope slides using 1:1 glycerol/PBS mounting medium. Fluorescent images of the cells were obtained using Olympus Fluorview FV1200 confocal microscope (Melville, NY USA) equipped with a bandpass filter for green emission (513-556 nm) and a 60X oil immersion lens (NA 1.35). Image J software (Version 1.50b, U.S. National Institute of Health, Bethesda, Maryland, USA) was used to process the image.

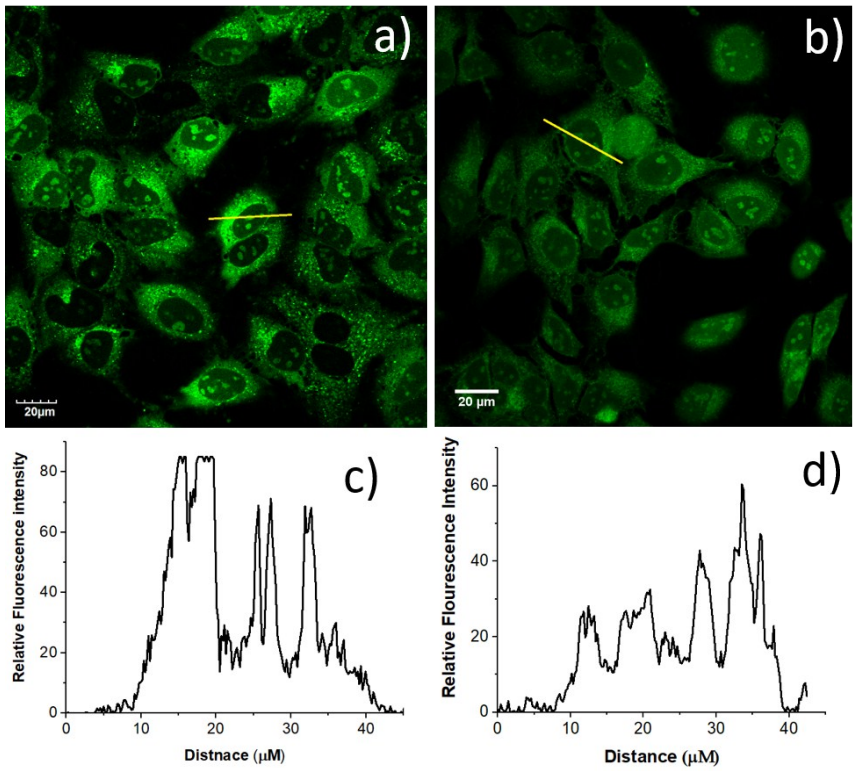


Figure S15. Confocal microscopic images of HeLa cells incubated with PEMC-3 (a) and PE trimer (b). The fluorescent intensity profiles (c and d) along the yellow lines in the confocal images indicate that PEMC-3 and PE trimer localize in the cytosol and nucleoli.

9. RNase and DNase digestion experiment:

In order to confirm the RNA selectivity of PEMCs, DNase and RNase digestion experiments were performed by following a literature procedure.[7] Briefly, cells were fixed by pure methanol for 1 min at room temperature followed by washing with PBS three times. The cell membrane was then permeabilized by adding 1 % Triton X-100 for 2 min, and then the cells were washed with PBS three times. Three wells were treated with 10 μM of PEMC-1, next three wells were treated with 10 μM of PEMC-2, and the rest three wells were treated with 10 μM of PE trimer. Cells were incubated at 37 °C in 5% CO_2 for 1 h. Then, cells were washed with PBS three times. To each well of three sets of samples, 100 μL of PBS (as control experiment), 30 μg/ml of DNase (Sigma), and 25 μg/ml DNase-free RNase (GE), respectively, were added and the wells were incubated at 37 °C in 5 % CO_2 for 2 h. Cells were rinsed by PBS three times before imaging.

10. Cell entry under non-energy dependent conditions:

Cells were pre-treated with 0.05% of sodium azide (NaN_3) in the presence of 2-deoxyglucose (25×10^{-3}M) for 15 min before PEMC treatment. Cells were incubated with 10 μM of PEMCs and PE trimer, respectively, for 1 h. Cells were washed three times with 1× PBS and fixed with 4 % PFA for 10 min. Cells were then washed three times with 1× PBS, and the coverslips were mounted on microscope slides using a 1:1 glycerol/PBS mounting medium. For incubation in 4 ^{o}C, the medium

of cells in a platewell was replaced with pre-cooled medium and PEMC in cooled medium was added to the cells. After incubation in 4 °C for 1 h, cells were washed and fixed for microscopic imaging.

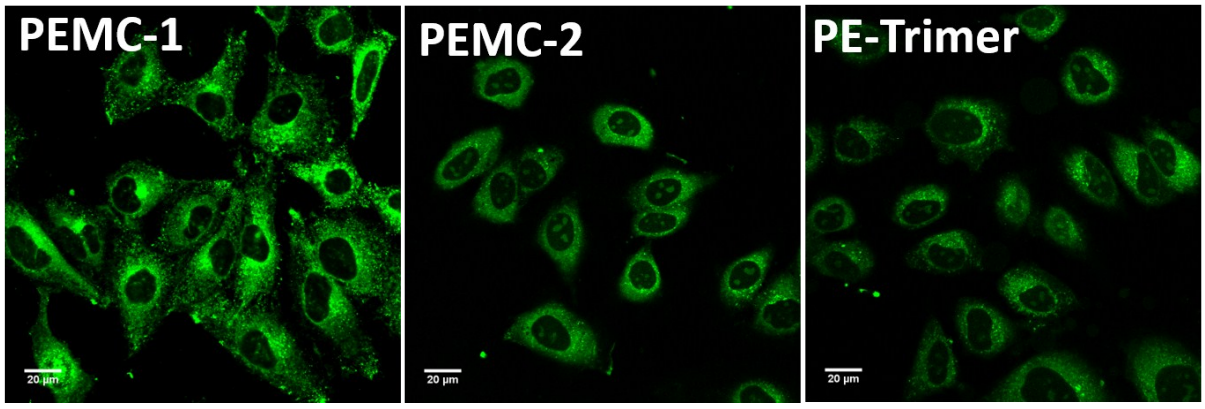


Figure S16. Fluorescence microscopic images of HeLa cells incubated with 10 µM PEMC-1, PEMC-2 and PE-Trimer for 1 h under ATP depletion condition.

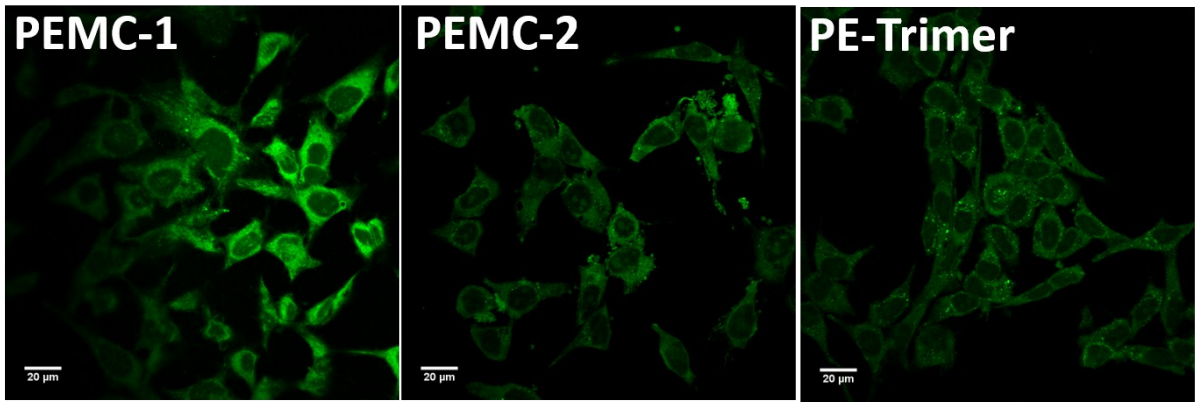


Figure S17. Fluorescence microscopic images of Hela cells incubated with 10 µM PEMC-1, PEMC-2 and PE-Trimer for 1 h under 4 °C.

11. Crystallographic Experimentation:

The compound crystallizes in monoclinic P21/c space group, with one half of the molecule in the asymmetric unit. The molecule features two intramolecular alkyne pi-phenyl pi interactions, with centroid to bond distances of 3.75 – 3.85 Å. A solvent water molecule is co-crystallized and forms hydrogen bonds with amine N (N—O distance 2.99 Å) and one of the ether O-atoms (O—O distance 2.92 Å).

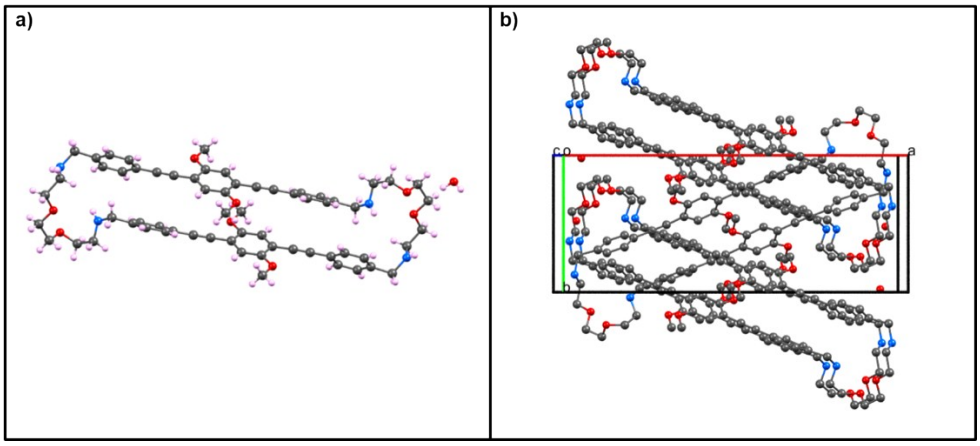


Figure S18. a) Molecular structure of PEMC-1; b) Crystal packing diagram viewed along the crystallographic c-axis. H-atoms are not shown for clarity.

Table S2. X-ray crystallographic data for **PEMC-1**.

PEMC-1	
Formula	$C_{64}H_{72}N_4O_{10}$
$D_{calc.}$/ g cm^{-3}	1.234
μ/mm^{-1}	0.083
Formula Weight	1057.25
Colour	colourless
Shape	plate
Size/mm^3	0.14×0.11×0.02
T/K	296(2)
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	25.344(2)
b/Å	10.0372(6)
c/Å	11.2060(7)
α/°	90
β/°	93.783(2)
γ/°	90
V/Å^3	2844.4(3)
Z	2
Z'	0.5
Wavelength/Å	0.710760
Radiation type	MoK_α
Θ_{min}/°	2.877
Θ_{max}/°	25.079
Measured Refl.	45860
Independent Refl.	5042
Reflections Used	1624
R_{int}	0.4283
Parameters	354
Restraints	0
Largest Peak	0.331
Deepest Hole	-0.228
GooF	0.997
wR_2 (all data)	0.2005
wR_2	0.1429
R_1 (all data)	0.3269
R_1	0.1007

12. Details of Theoretical Simulations

The theoretical structure of the PE-Trimer and PEMC-2 systems were first created using MolView[8] before being optimized in vacuum using the density-functional tight-binding (DFTB) method, including Grimme D3-type dispersion with Becke-Johnson damping (D3-BJ)[9] and the 3ob parameter set. DFTB is an approximate density functional theory (DFT) method based approach utilizing an empirical tight-binding framework and an optimized minimal LCAO Slater-type all-valence basis set in combination with a two-center approximation for Hamiltonian matrix

elements. The Coulombic interaction between partial atomic charges was determined using the self-consistent charge (SCC) formalism from third order DFTB (DFTB3), with van der Waals and dispersion interactions being described by Grimme D3-BJ. All vacuum calculations were carried out with the DFTB+ program package version 17.1 with the default convergence criteria for density and geometry optimization procedures. Molecular dynamics calculations were carried to locate global minimum structures were located using DFTB3-D3(BJ) and the Nose-Hoover (NVT) thermostat. The time step and temperature used were 0.4 fs and 298.15 K, respectively, with geometries extracted every 0.52 ps. The final structure was reoptimized using implicit water with the C-PCM approach as implemented in GAMESS-US (see Fig. 3 in the main text and Table S5 for the Cartesian coordinates).

Table S3. Excitation energies in eV and oscillator strengths (arb. Units) above 0.005 for PE-Trimer. Transition refers to the orbital number (HOMO: 141, LUMO: 142), weight refers to the weight of the particular orbital excitation in the respective state.

ω [eV]	Osc. Str.	Transition	Weight
2.637	0.6654	141 -> 142	1.000
3.499	0.7913	140 -> 142	1.000
3.979	0.0848	141 -> 146	0.965
4.023	0.0229	136 -> 142	0.988
4.044	0.0094	135 -> 142	0.999
4.347	0.2439	137 -> 143	0.910
4.484	0.0069	128 -> 142	0.991
4.644	0.0932	129 -> 142	0.780

Table S4. Excitation energies in eV and oscillator strengths (arb. Units) above 0.005 for PEMC-2. Transition refers to the orbital number (HOMO: 256, LUMO: 257), weight refers to the weight of the particular orbital excitation in the respective state.

ω [eV]	Osc. Str.	Transition	Weight
2.403	0.1438	253 -> 258	0.992
2.599	0.0061	251 -> 257	1.000
2.642	0.0108	251 -> 258	0.999
2.652	0.1851	252 -> 257	0.963
2.910	0.0085	250 -> 258	0.853
2.928	0.0177	253 -> 260	0.893
2.952	0.0068	253 -> 259	0.812
2.963	0.2109	250 -> 257	0.828
3.008	0.0503	248 -> 257	0.988
3.120	0.0348	247 -> 257	0.982
3.142	0.0541	247 -> 258	0.852
3.160	0.0148	246 -> 257	0.989
3.194	0.2990	248 -> 258	0.762
3.196	0.0052	246 -> 258	1.000
3.199	0.0084	245 -> 257	0.862
3.221	0.0149	245 -> 258	0.938

3.269	0.0415	252 -> 260	0.949
3.382	0.0248	243 -> 258	0.999
3.395	0.0850	252 -> 261	0.989

Table S5. Cartesian coordinates of PE-trimer and PEMC-2 ions in their protonated form with 4 and 8 positive charges, respectively, optimized using the DFTB3-D3(BJ)/3ob/C-PCM method.

PE-trimer:

```
110
FINAL RDFTB ENERGY = -125.4816162392, GRIMME'S DISPERSION ENERGY = -
0.0864296646
C   8.0179668527  -0.7063945268  -0.9521338817
C   6.5059452891  -0.6950174539  -1.0218879294
C   5.8429025445  -1.2748329242  -2.1137360588
C   4.4528616302  -1.3107758232  -2.1567384250
C   3.6968805620  -0.7628623225  -1.1023829005
C   4.3648059905  -0.1582250176  -0.0201274587
C   5.7551732364  -0.1255631011   0.0167150173
C   2.2646445156  -0.8512780588  -1.1047242968
C   1.0543732799  -0.9784505752  -1.0317247148
C  -0.3620925184  -1.1648482709  -0.9305531183
C  -1.0404756914  -1.9846200000  -1.8711947958
C  -2.4147285451  -2.2207766222  -1.7342313119
C  -3.1293914023  -1.6503881231  -0.6608126231
C  -2.4572555991  -0.8053675495   0.2616045810
C  -1.0822610618  -0.5734297144   0.1283930771
C  -0.9267505829  -3.3522788098  -3.8403459367
C  -2.6135935764   0.6644952980   2.1582637404
C  -4.5273704184  -1.9145180222  -0.4977000682
C  -5.7113383072  -2.1533178525  -0.3329974878
C  -7.1174671652  -2.3868170101  -0.1664732168
C  -7.8578389780  -3.0336391312  -1.1743813395
C  -9.2284660161  -3.2230787625  -1.0257615961
C  -9.8872645288  -2.7719540832   0.1266521485
C  -9.1490050046  -2.1436543152   1.1405824434
C  -7.7794358534  -1.9493749545   0.9972997385
C -11.3837196562  -2.9458711922   0.2729196768
C -11.3143311955  -5.4273459214   0.6097040181
C -12.1077371862  -6.5222568003   1.3336842864
C -14.3004760603  -6.1448140950   2.3630057282
C  12.3045678038   0.7778150469  -2.0895544763
C -15.1775967131  -4.9056701115   2.2681738095
C  11.5820339318   2.0648007027  -2.4579416708
C   9.2804373272   2.7325389884  -1.9391731867
C   8.2397548233   1.7483818814  -1.3890808635
H   6.4260574304  -1.7212468682  -2.9122270247
H   3.9464215320  -1.7765981280  -2.9946212437
H   3.7910433575   0.2655851238   0.7959836423
H   6.2692025954   0.3247849909   0.8603497573
H  -2.9470271264  -2.8558147992  -2.4319133204
H  -0.5493954714   0.0524234043   0.8341069498
H  -1.3800269722  -4.2254905143  -3.3399034054
H  -1.7443281579  -2.7975371955  -4.3318698406
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H	-1.8388152471	0.1534307004	2.7556904497
H	-2.1128347114	1.4692842051	1.5942523692
H	8.3634230605	-0.5300453846	0.0689378494
H	8.4289484657	-1.6570384910	-1.3015213600
H	-7.3585416601	-3.3757544822	-2.0734609177
H	-9.8009359981	-3.7087416119	-1.8103933379
H	-9.6579333244	-1.8009560066	2.0357932760
H	-7.2187388209	-1.4532437458	1.7820173791
H	-11.8461114635	-2.0607452128	0.7178680245
H	-11.8521712202	-3.1452972416	-0.6928748951
H	-10.2345135261	-5.5467205643	0.7140562414
H	-11.5564739904	-5.4217690374	-0.4565865531
H	-11.8844180260	-7.5013083382	0.8860940473
H	-11.8427687975	-6.5530636032	2.4007640088
H	-13.6509805300	-6.0978022200	3.2492960338
H	12.7398837627	0.8510996594	-1.0803939761
H	-14.9186847149	-7.0548005455	2.4370290141
H	13.1195175529	0.5702114328	-2.8010620554
H	-15.8003606201	-4.9416367736	1.3601671181
H	11.1226788848	1.9810491310	-3.4537530425
H	-15.8468997264	-4.8309938566	3.1399243122
H	12.2817971443	2.9162387947	-2.4696376005
H	9.0676208992	3.7455747702	-1.5689627426
H	9.2587983391	2.7452917213	-3.0383457711
H	8.2333756246	1.7696639701	-0.2959484660
H	7.2283179769	1.9552138068	-1.7429497441
N	8.6135171768	0.3663393650	-1.8114592292
N	-11.7074046211	-4.1017786875	1.1700717990
O	-0.2809857805	-2.5186243985	-2.8758243670
O	-3.2233134908	-0.2584798607	1.2535018432
O	-13.4909152901	-6.2089012608	1.1721629994
O	11.3575039285	-0.2986467285	-2.1184111600
O	10.5575584084	2.2975696137	-1.4704680506
O	-14.3302761325	-3.7502468819	2.2115719246
C	0.1105613298	-3.7919685355	-4.8586950754
H	0.5778170859	-2.9196934406	-5.3509605972
H	0.9239354971	-4.3674742466	-4.3807227417
C	-3.7075047250	1.2324231057	3.0453331547
H	-4.4828717948	1.7337083346	2.4383046938
H	-4.2113012132	0.4336688316	3.6188026430
O	-0.5505432114	-4.6024130498	-5.8354771882
O	-3.1168408108	2.1748613043	3.9462136161
C	0.3285840749	-5.0948631337	-6.8349797714
H	0.8473970497	-4.2594509493	-7.3398951425
H	1.0992733852	-5.7478703735	-6.3845886321
C	-4.0735794297	2.7710348662	4.8092692919
H	-4.5889643162	1.9931415780	5.4032143199
H	-4.8424299732	3.3081460697	4.2235115332
C	-3.3288600733	3.7340569038	5.7325166171
H	-2.5640268317	3.2045824951	6.3036514856
H	-2.8379085974	4.5253460333	5.1633560351
C	-0.5215980637	-5.8790917854	-7.8340156483
H	-1.0363242140	-6.7044433854	-7.3381770879
H	-1.2775755668	-5.2342009435	-8.2861281681

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N  -4.2575882641   4.3655523007   6.6977771417
N   0.3067337169  -6.4478079870  -8.9217356447
H -14.8845131409  -2.9599656619   2.1241204804
H -11.2367646670  -3.9635163134   2.0726824520
H   8.3151923446   0.2195569771  -2.7830416884
H  11.7992736216  -1.1157893637  -1.8418330774
H  -4.7353617156   3.6545345760   7.2572551584
H  -4.9709979882   4.9187287383   6.2158406416
H   1.0011609765  -7.0997394369  -8.5483165778
H  -0.2740609721  -6.9609135512  -9.5886457725
H   0.8043372061  -5.7140946924  -9.4329029252
H  -3.7567979472   4.9856556728   7.3386585190
H -12.7447679780  -4.1117718235   1.3711932002
H   9.6663527297   0.2759818830  -1.7929770988
```

PEMC-2:

```
200
FINAL RDFTB ENERGY = -226.3105528671, GRIMME'S DISPERSION ENERGY = -
0.2477290447
C   2.4582047578  -0.4484732241  -0.7001239049
C   1.5133931829  -0.2087523425  -1.7180125192
C   1.3738371863   1.0448156865  -2.3300969076
O   0.3831833720   1.1187824561  -3.2681596188
C  -0.0787413439   2.3788390112  -3.7551553376
C  -1.4079218929   2.1366743555  -4.4674698285
O  -2.0009700536   3.3767906924  -4.8838541603
C  -2.6682411594   4.1090513717  -3.8663788748
C  -3.7731381985   4.9161200996  -4.5563513666
C   2.2399684491   2.1068817565  -1.9471774050
C   3.1850834339   1.8643469096  -0.9279508292
C   3.3138462568   0.6186991636  -0.3062070460
O   4.2232972221   0.5697020501   0.7243991954
C   5.0140218150  -0.6061555027   0.9678940106
C   5.8070853975  -1.0439943193  -0.2663743136
O   5.0159023006  -1.9798960606  -1.0245976643
C   5.7448794403  -2.9973197232  -1.7042400687
C   4.7495712131  -4.1304809614  -1.9563313456
C   2.2093502646   3.4167596692  -2.5235947166
C   2.2921161232   4.5676996452  -2.9218185046
C   2.1488597733   5.8623568832  -3.5185708022
C   0.9493856583   6.1851711651  -4.1875901321
C   0.7992755891   7.4279303333  -4.7940034474
C   1.8274703183   8.3848874984  -4.7351589670
C   3.0105654798   8.0714544713  -4.0483255454
C   3.1727443129   6.8239823109  -3.4502249382
C   1.6097154118   9.7023925347  -5.4498876513
N   2.7912152832  10.6006360870  -5.3674143359
H   2.9969657909  10.7816487828  -4.3722889431
C   2.5836146174  11.9291013696  -6.0105300549
C   1.5400990940  12.7291420590  -5.2246846822
O   1.5895163394  12.3021882385  -3.8570697033
C   0.8126773783  13.1699507722  -2.9965828383
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C   0.8457145581  12.6321217094  -1.5692064365
O  -0.2622726669  11.7488253239  -1.2971095528
C  -0.2425698929  10.5152966606  -1.9958888436
C   0.9156541260   9.6148352132  -1.4847064688
N   0.4862687242   8.1897636440  -1.3291390911
H   0.3598588393   7.7662708224  -2.2620495833
C   1.4718439121   7.3760832159  -0.5548979706
C   1.0085641965   5.9568516164  -0.3014768505
C   1.7626246125   5.1823417935   0.5961649203
C   1.4008573427   3.8723841088   0.8795023822
C   0.2621474308   3.3051485880   0.2746506876
C  -0.4925064103   4.0769738121  -0.6253485746
C  -0.1163052356   5.3880936199  -0.9151659432
C  -0.0718834025   1.9385052834   0.5641483083
C  -0.1682440863   0.7592951028   0.8625072901
C  -0.4028914068  -0.6324507173   1.1215818729
C   0.0061749755  -1.2610515037   2.3272112046
C  -0.3307370695  -2.5937487769   2.5802763718
C  -1.0053408867  -3.3656183568   1.6157302635
C  -1.3671971041  -2.7541264122   0.3870150627
C  -1.0875747621  -1.4052669996   0.1563852147
O  -1.9504366945  -3.4849652325  -0.6311813968
C  -3.3058592851  -3.9305029193  -0.3885059716
C  -4.2605319245  -2.7432503846  -0.4186075200
O  -4.2751741808  -2.1134083157   0.8807231940
C  -5.1549049697  -0.9832034410   0.9406520807
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