Electronic Supplementary Information

Synthesis of trifluoroethoxy-coated binuclear phthalocyanines with click spacers and investigations of their clamshell behaviour

Hideyuki Yoshiyama, Norio Shibata,* Takefumi Sato, Shuichi Nakamura, Takeshi Toru

Department of Frontier Materials, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso, Showa-ku, Nagoya 466-8555, Japan

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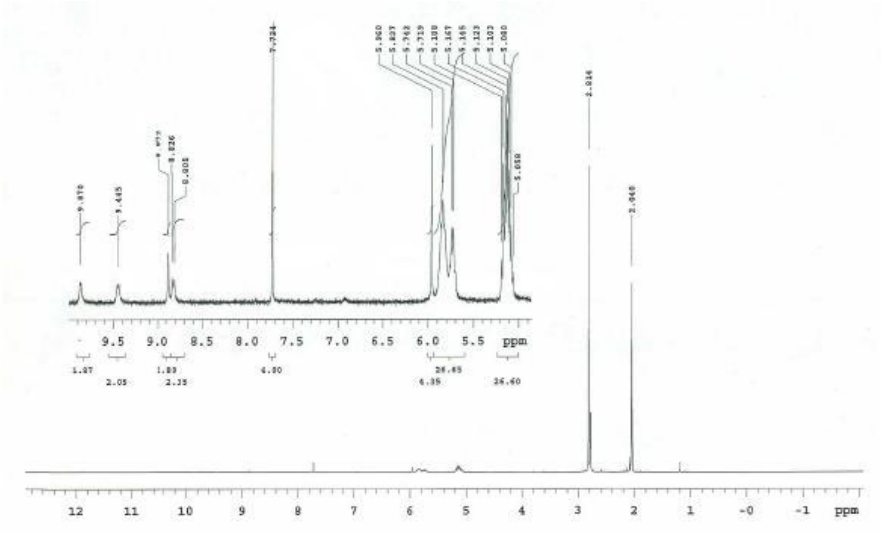


Fig. S1 ^{1}H NMR spectra of **1** (400 MHz in acetone-d_6).

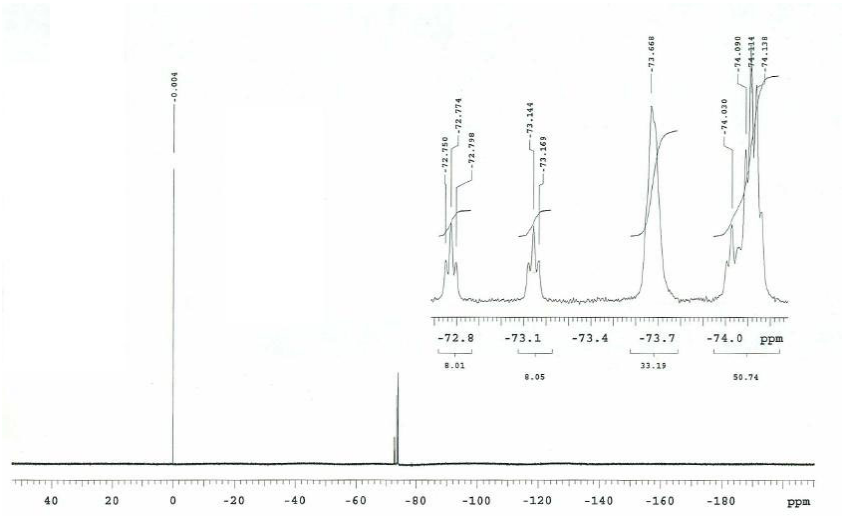


Fig. S2 ^{19}F NMR spectra of **1** (376 MHz in acetone-d_6).

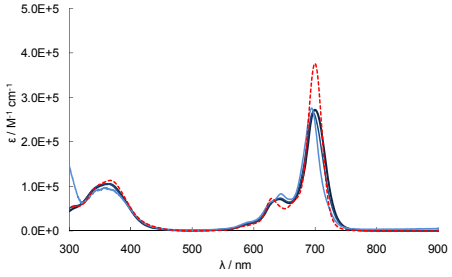


Fig. S3 UV-vis spectra of **1** in $PhCF_3$ (deep to light blue solid lines: 0.5 x 10^{-4} to 10^{-6} M, red dotted line: with 1 vol% of pyridine).

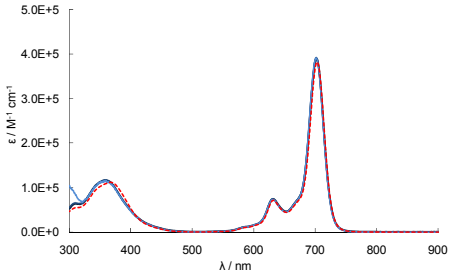


Fig. S4 UV-vis spectra of **1** in dioxane (deep to light blue solid lines: 0.5 x 10^{-4} to 10^{-6} M, red dotted line: with 1 vol% of pyridine).

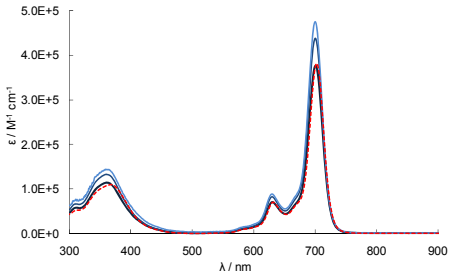


Fig. S5 UV-vis spectra of **1** in THF (deep to light blue solid lines: 0.5 x 10^{-4} to 10^{-6} M, red dotted line: with 1 vol% of pyridine).

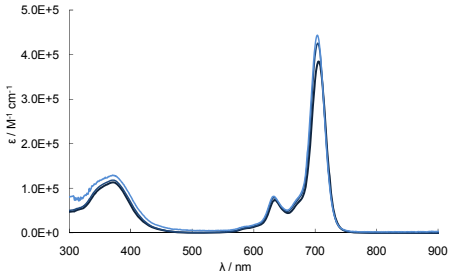


Fig. S6 UV-vis spectra of **1** in pyridine (deep to light blue solid lines: 0.5 x 10^{-4} to 10^{-6} M).

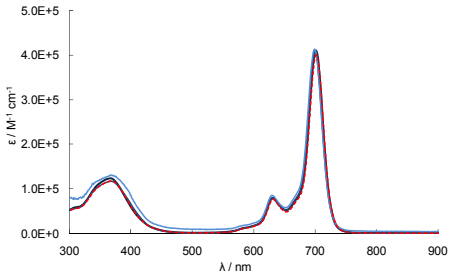


Fig. S7 UV-vis spectra of **1** in DMF (deep to light blue solid lines: 0.5 x 10^{-4} to 10^{-6} M, red dotted line: with 1 vol% of pyridine).

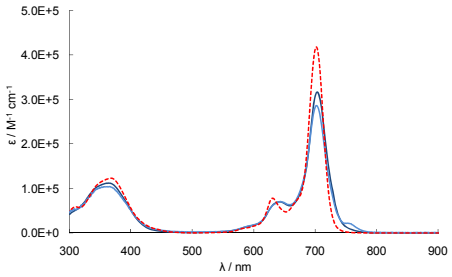


Fig. S8 UV-vis spectra of **1** in CH_2Cl_2 (deep to light blue solid lines: 0.5 x 10^{-5} to 10^{-6} M, red dotted line: with 1 vol% of pyridine).

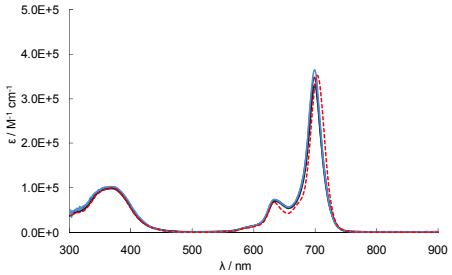


Fig. S9 UV-vis spectra of **1** in PhCN (deep to light blue solid lines: 0.5 x 10^{-4} to 10^{-6} M, red dotted line: with 1 vol% of pyridine).

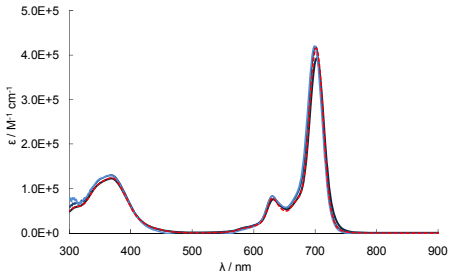


Fig. S10 UV-vis spectra of **1** in *m*-$C_6H_4F_2$ (deep to light blue solid lines: 0.5 x 10^{-4} to 10^{-6} M, red dotted line: with 1 vol% of pyridine).

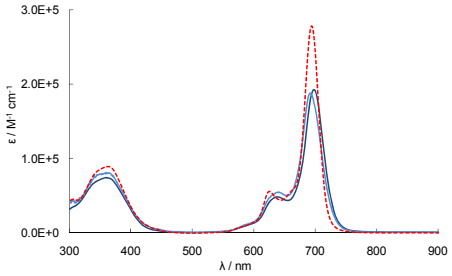


Fig. S11 UV-vis spectra of **1** in Solkane® ($CF_3CH_2CF_2CH_3$) (deep to light blue solid lines: 0.5 x 10^{-4} to 10^{-6} M, red dotted line: with 1 vol% of pyridine).

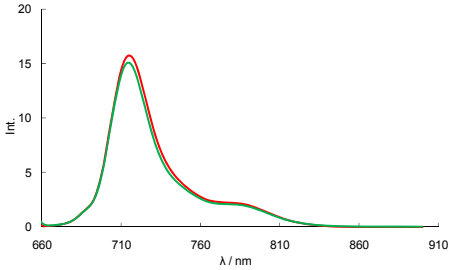


Fig. S12 Steady-state fluorescence spectra of **1** (red: dioxane, green: $CHCl_3$).

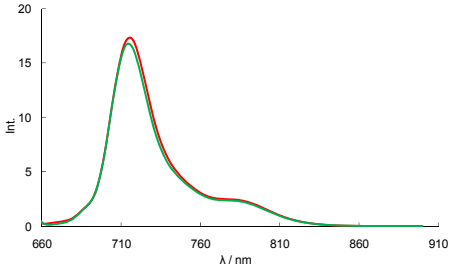


Fig. S13 Steady-state fluorescence spectra of **2** (red: dioxane, green: $CHCl_3$).

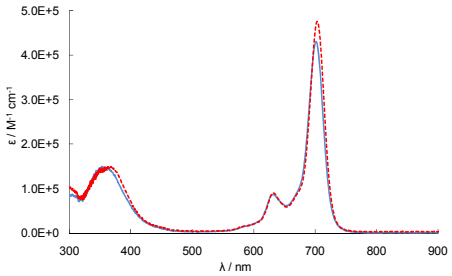


Fig. S14 UV-vis spectra of **6** in $CHCl_3$ (light blue: 3.0 x 10^{-7} M, red dotted: with 1 vol% of pyridine).

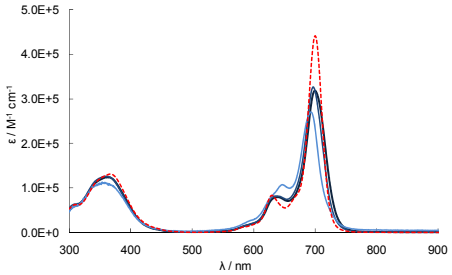


Fig. S15 UV-vis spectra of **6** in $PhCF_3$ (deep to light blue solid lines: 0.5 x 10^{-4} to 10^{-6} M, red dotted line: with 1 vol% of pyridine).

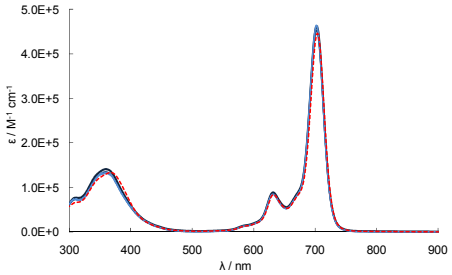


Fig. S16 UV-vis spectra of **6** in dioxane (deep to light blue solid lines: 0.5 x 10^{-4} to 10^{-6} M, red dotted line: with 1 vol% of pyridine).

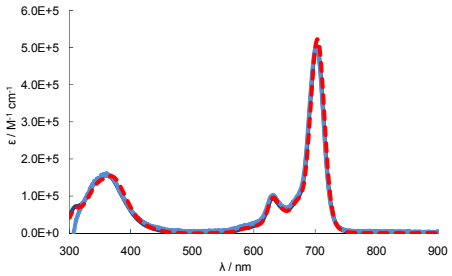


Fig. S17 UV-vis spectra of **7** in $CHCl_3$ (blue: 2.2 x 10^{-6} M and light blue: 2.2 x 10^{-7} M, red dotted: with 1 vol% of pyridine).

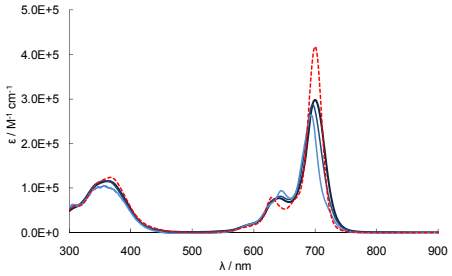


Fig. S18 UV-vis spectra of **7** in $PhCF_3$ (deep to light blue solid lines: 0.5 x 10^{-4} to 10^{-6} M, red dotted line: with 1 vol% of pyridine).

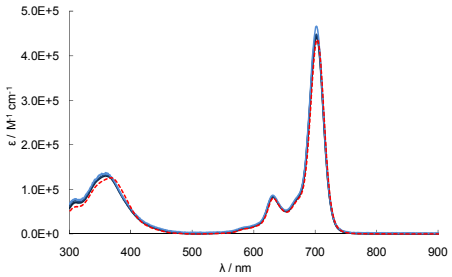


Fig. S19 UV-vis spectra of **7** in dioxane (deep to light blue solid lines: 0.5 x 10^{-4} to 10^{-6} M, red dotted line: with 1 vol% of pyridine).

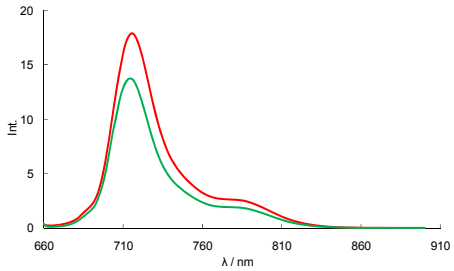


Fig. S20 Steady-state fluorescence spectra of **6** (red: dioxane, green: $CHCl_3$).

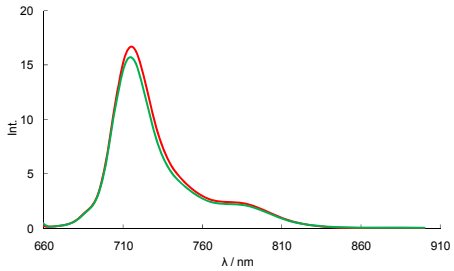


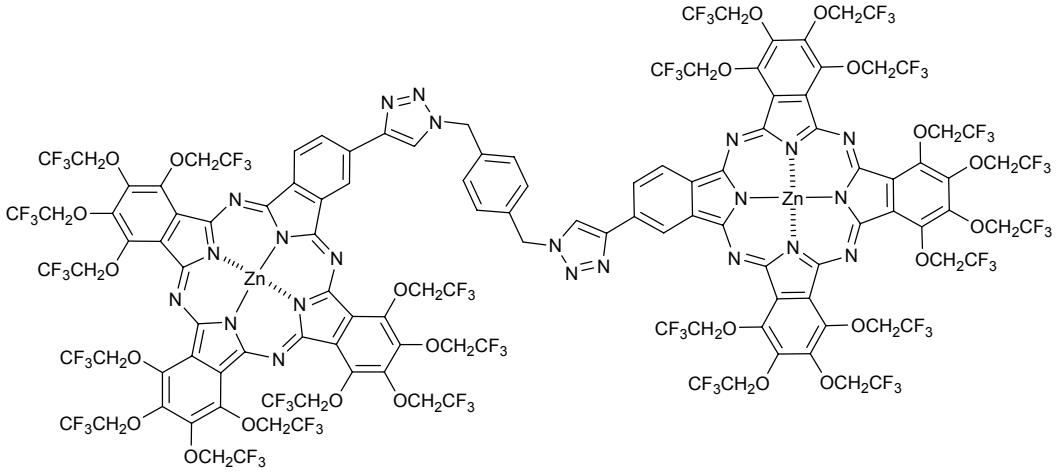
Fig. S21 Steady-state fluorescence spectra of **7** (red: dioxane, green: $CHCl_3$).

Experimental Section

General

All solvents were dried and distilled according to standard procedures. All of the reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica-gel plate (60F-254). Column chromatography was carried out on a column packed with silica gel 60N spherical neutral size 63-210 μm. ^{1}H NMR (200/400 MHz), ^{13}C NMR (50 MHz) and ^{19}F NMR (188/376 MHz) spectra were taken on Varian Gemini-200 or Gemini-400 spectrometers. Chemical shifts are expressed in ppm downfield from internal standard tetramethylsilane (or acetone-d_6) for ^{1}H or ^{13}C, and $CFCl_3$ for ^{19}F NMR. Infrared (IR), UV-vis and steady-state fluorescence spectra were recorded on a JASCO FT/IR-200 spectrometer, V-530 spectrometer and FP-6200 Fluorospectrometer, respectively. Quantum yields were calculated following the procedure mentioned before.[1] Mass spectra of ESI and MALDI-TOF were taken on SHIMADZU LCMS-2010 EV, and Axima CFR plus, respectively. Reverse phase HPLC analyses were performed on JASCO PU-2080 Plus using 4.6 x 250 mm Develosil ODS-HG-5 column and MD-2015 multiwavelength detector. Electrochemical experiments were carried out on a BAS 50W electrochemical analyzer (Bioanalytical Systems, Inc., West Lafayette, IN 47906, USA). Tetrabutylammonium hexafluorophosphate (TBAPF) was purchased from TCI and recrystallized from EtOH. The solvent THF (Kanto Chemical Co. Inc., tetrahydrofuran, dehydrated stabilizer free) was passed through Glass Contour Ultimate Solvent System. For CV and DPV, 3 mm platinum was used as a working electrode and platinium wire as a counter electrode. $Ag/AgNO_3$ (0.01 M in MeCN/0.1 M TBAPF) was used as a reference electrode separated by vycor glass, and all potentials given relate to this electrode. The measurements were performed using a concentration of approximately 0.5 mM of the compounds. 23-ethynyl-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate zinc (II) (**3**)[2], 1,3-bis(azidomethyl)benzene (**4b**)[3] and 1,4-bis(azidomethyl)benzene (**4c**)[3] were prepared by the method described previously.

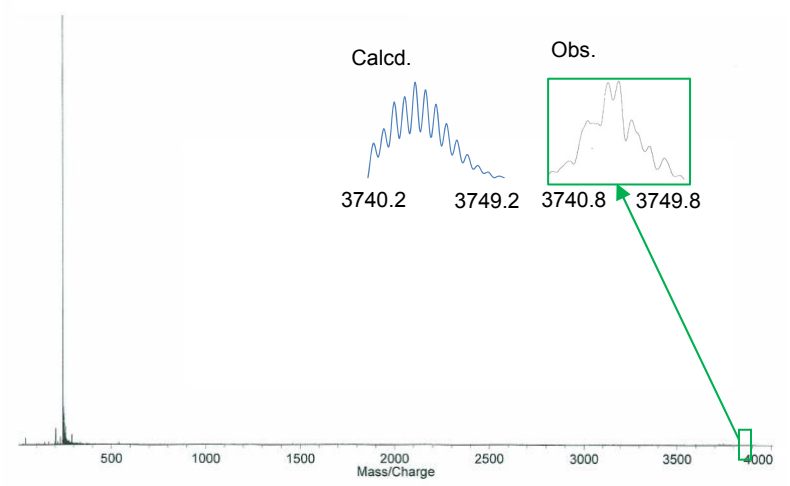
1,4-Bis(1-(dodekakistrifluoroethoxyphthalocyaninate zinc(II))-1*H*-1,2,3-triazol-4-yl)benzene (**1**)



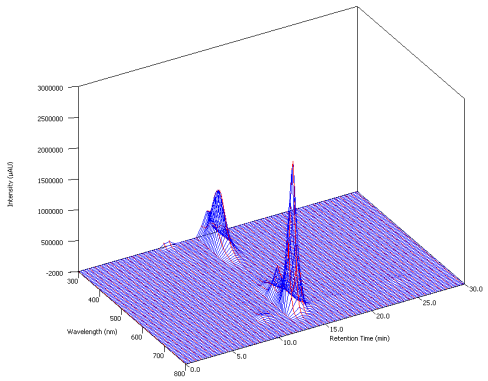
A mixture of 23-ethynyl-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate zinc (II) (**3**)[2] (44.9 mg, 0.025 mmol), 1,4-bis(azidomethyl)benzene (**4a**)[3] (1.9 mg, 0.010 mmol), CuI (1.0 mg, 0.005 mmol) Et_3N (0.05 ml) and DMSO (1.0 ml) was freeze dried to remove oxygen. The solution was stirred at 60 °C for 2 h. After cooling it to rt, water and dil. sulfuric acid were added and the precipitates were filtered. Purification by silica gel column chromatography (hexane : acetone = 70 : 30 to 60 : 40) gave green solids. 36.0 mg, 95%.

$C_{124}H_{64}F_{72}N_{22}O_{24}Zn_2$; M.W.: 3744.63, ^{1}H-NMR (acetone-d_6, 400 MHz): δ 5.06-5.19 (m, 24H), 5.72-5.85 (m, 24H), 5.96 (s, 4H), 7.72 (s, 4H), 8.82 (d, J = 8.4 Hz, 2H), 8.87 (s, 2H), 9.45 (d, J = 8.4 Hz, 2H), 9.87 (s, 2H); ^{19}F-NMR (acetone-d_6, 376 MHz): δ –74.1- –74.0, –73.7, –73.1, –72.8; IR (KBr): 2975, 1488, 1456, 1275, 1159, 1068, 1008, 970, 860, 762, 670 cm^{-1}; UV-vis (2.6 x 10^{-6} M in $CHCl_3$): λ_{max} (log ε) = 702 (5.61), 631 (4.89), 360 (5.11) nm; (0.5 x 10^{-6} M in $PhCF_3$): λ_{max} (log ε) = 695 (5.44), 644 (4.92), 358 (4.99) nm; (0.5 x 10^{-6} M in dioxane): λ_{max} (log ε) = 703 (5.62), 632 (4.90), 368 (5.10) nm; (0.5 x 10^{-6} M in THF): λ_{max} (log ε) = 700 (5.68), 630 (4.95), 358 (5.16) nm; (0.5 x 10^{-6} M in pyridine): λ_{max} (log ε) = 704 (5.66), 632 (4.99), 370 (5.18) nm; (0.5 x 10^{-6} M in DMF): λ_{max} (log ε) = 699 (5.62), 630 (4.93), 368 (5.12) nm; (0.5 x 10^{-6} M in CH_2Cl_2): λ_{max} (log ε) = 702 (5.46), 643 (4.85), 365 (5.02) nm; (0.5 x 10^{-6} M in PhCN): λ_{max} (log ε) = 699 (5.56), 633 (4.86), 369 (5.01) nm; (0.5 x 10^{-6} M in m-PhF_2): λ_{max} (log ε) = 699 (5.62), 630 (4.92), 364 (5.11) nm; (0.5 x 10^{-6} M in Solkane): λ_{max} (log ε) = 692 (5.27), 640 (4.73), 361 (4.91) nm; Fluorescence ($CHCl_3$): λ_{em} = 715 nm, Φ_f = 0.24, (dioxane): λ_{em} = 715 nm, Φ_f = 0.26.

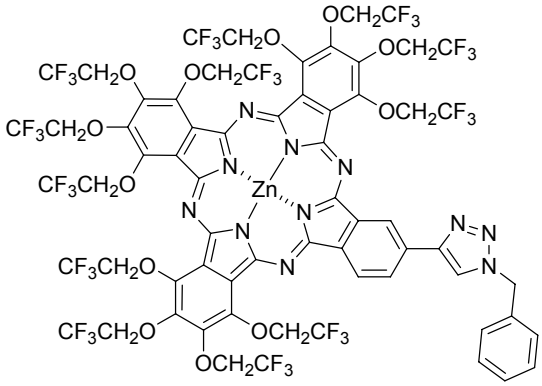
MALDI-TOF MS (dithranol): m/z = 3740.8-3749.8 ([M$^+$], isotopic pattern)



HPLC: (H_2O:MeCN:THF = 8:42:50, 0.3 ml/min), t_R = 14.0 min.



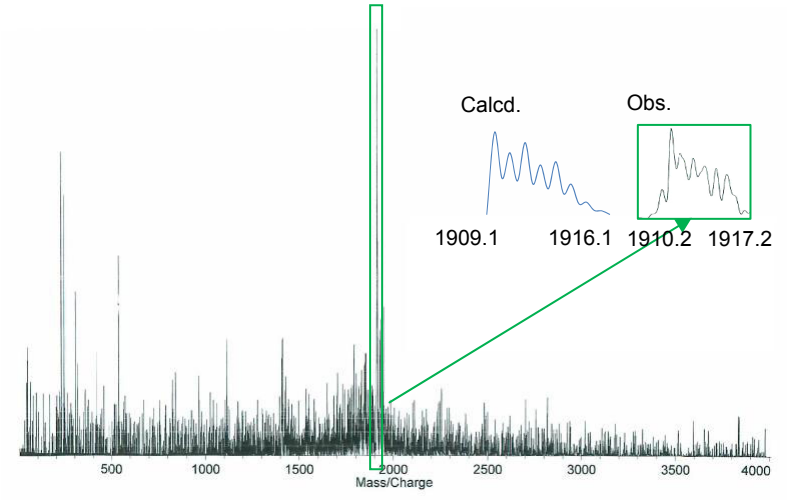
23-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate zinc (II) (**2**)



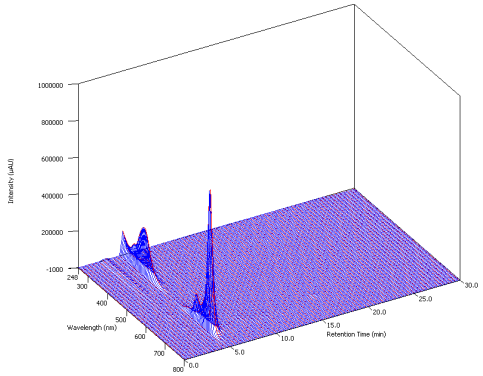
A mixture of **3** (45.3 mg, 0.255 mmol), benzylazide **4b** (17.1 mg, 0.128 mmol), CuI (1.0 mg, 0.005 mmol), Et_3N (0.05 ml) and DMSO (0.8 ml) was freeze dried to remove oxygen, and stirred at 60 °C for 2 h. After cooling it to rt, water and dil. sulfuric acid were added and the precipitates were filtered. Purification by silica gel column chromatography (hexane : acetone = 70: 30 to 65 : 35) gave green solids. 40.2 mg, 83%.

$C_{65}H_{35}F_{36}N_{11}O_{12}Zn$; M.W.: 1911.37; ^{1}H-NMR (acetone-d_6, 200 MHz): δ 4.9-5.3 (brm, 14H), 5.6-6.1 (brm, 12H), 7.45 (br, 5H), 8.56 (brm, 2H), 9.35 (brm, 1H); ^{19}F-NMR (acetone-d_6, 188 MHz): δ –73.9, –73.6, –73.1, –72.6; IR (KBr): 2969, 2574, 1488, 1430, 1275, 1159, 1068, 1009, 970, 852, 662 cm^{-1}; UV-vis (1.0 x 10^{-6} M in $CHCl_3$): λ_{max} (log ε) = 702 (5.33), 630 (4.60), 360 (4.83) nm; (1.0 x 10^{-6} M in $PhCF_3$): λ_{max} (log ε) = 697 (5.33), 627 (4.58), 368 (4.75) nm; (1.0 x 10^{-6} M in dioxane): λ_{max} (log ε) = 702 (5.35), 631 (4.62), 360 (4.84) nm; Fluorescence ($CHCl_3$): λ_{em} = 715 nm, Φ_f = 0.27, Fluorescence (dioxane): λ_{em} = 715 nm, Φ_f = 0.30.

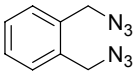
MALDI-TOF MS: *m/z* = 1910.2-1917.2 ([M+H$^+$], isotopic pattern)



HPLC: (H_2O:MeCN:THF = 11:54:35, 1.0 ml/min), t_R = 5.1 min.



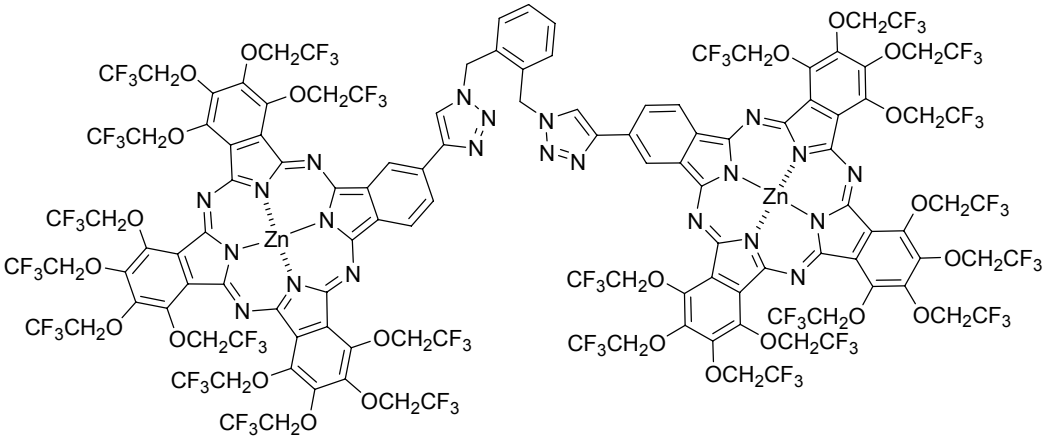
1,2-Bis(azidomethyl)benzene (5a)



A mixture of 1,2-bis(bromomethyl)benzene (5.00 g, 18.9 mmol), sodium azide (2.96 g, 45.5 mmol) was dried under vacuum for 1 h. To this mixture dry DMF (10 ml) was added under nitrogen. The reaction mixture was allowed to stir for 5 h at 60 °C. The solvent was added with water, and extracted with diethyl ether. The organic layer was washed with water and brine, dried over Na_2SO_4 and evaporated to dryness. The obtained oil was purified by silica gel column chromatography (hexane) to afford yellow liquid (3.53 g, 99%).

^{1}H NMR (200 MHz, $CDCl_3$) δ 4.37 (brs, 4H, Ar-*H*), 7.32 (s, 4H, C*H*$_2$); ^{13}C NMR (50 MHz, $CDCl_3$) 52.1, 128.6, 130.0, 133.5; IR (neat) ν/cm^{-1} 3307, 3027, 2941, 2888, 2098, 1604, 1492, 1455, 1347, 1252, 1178, 883, 756, 678; ESI-MS (MeOH/water) 187.70 [M$^-$], 160.70 [M-N_2^-]; *Anal. Calcd* for $C_8H_8N_6$: C, 51.06; H, 4.28; N, 44.66. Found: C, 51.16; H, 3.95; N, 44.70.

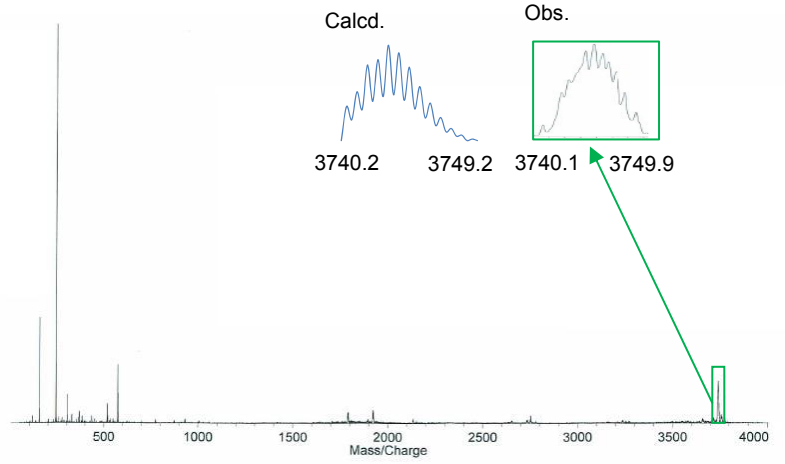
1,2-Bis(1-(dodekakistrifluoroethoxyphthalocyaninate zinc(II) yl)-1*H*-1,2,3-triazol-4-yl)benzene (6)



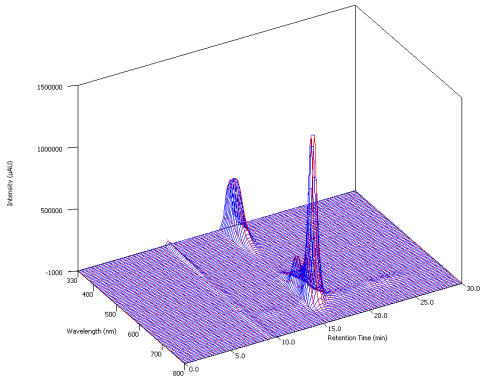
A mixture of **3** (40.2 mg, 0.0226 mmol), 1,2-bis(azidomethyl)benzene **5a** (1.7 mg, 0.009 mmol), CuI (1.0 mg, 0.005 mmol), Et_3N (0.05 ml) and DMSO (0.8 ml) was freeze dried to remove oxygen, and stirred at 60 °C for 2 h. After cooling it to rt, water and dil. sulfuric acid were added and the precipitates were filtered. Purification by silica gel column chromatography (hexane : acetone = 70: 30 to 60 : 40) gave green solids. 32.1 mg, 95%.

$C_{124}H_{64}F_{72}N_{22}O_{24}Zn_2$; M.W.: 3744.63; ^{1}H-NMR (acetone-d_6, 400 MHz): δ 5.08-5.20 (m, 24H), 5.73-5.93 (m, 24H), 6.30 (s, 4H), 7.61-7.66 (m, 4H), 8.88 (d, J = 8.1 Hz, 2H), 8.95 (s, 2H), 9.51 (d, J = 8.1 Hz, 2H), 9.91 (m, 2H); ^{19}F-NMR (acetone-d_6, 376 MHz): δ –74.1- –74.0, –73.7, –73.1, –72.7; IR (KBr): 2981, 1619, 1486, 1430, 1275, 1159, 1068, 971, 854, 664 cm^{-1};UV-vis (0.3 x 10^{-6} M in $CHCl_3$): λ_{max} (log ε) = 702 (5.63), 631 (4.94), 353 (5.17) nm; UV-vis (0.5 x 10^{-6} M in $PhCF_3$): λ_{max} (log ε) = 693 (5.43), 647 (5.03), 354 (5.05) nm; UV-vis (0.5 x 10^{-6} M in dioxane): λ_{max} (log ε) = 702 (5.68), 631 (4.93), 361 (5.13) nm; Fluorescence ($CHCl_3$): λ_{em} = 714 nm, Φ_f = 0.22, (dioxane): λ_{em} = 716 nm, Φ_f = 0.31.

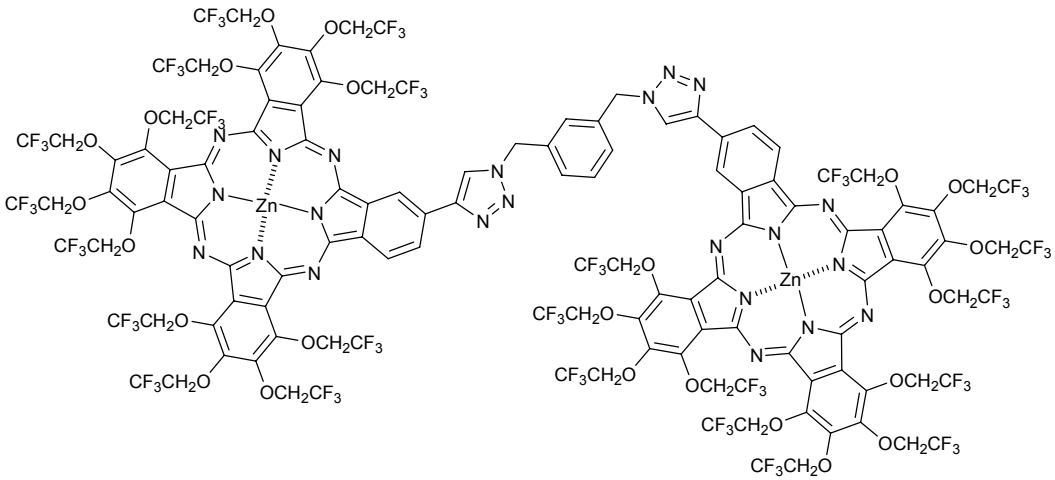
MALDI-TOF MS (dithranol): *m/z* = 3740.1-3749.9 ([M$^+$], isotopic pattern)



HPLC: (H_2O:MeCN:THF = 8:42:50, 0.3 ml/min), t_R = 16.5 min.



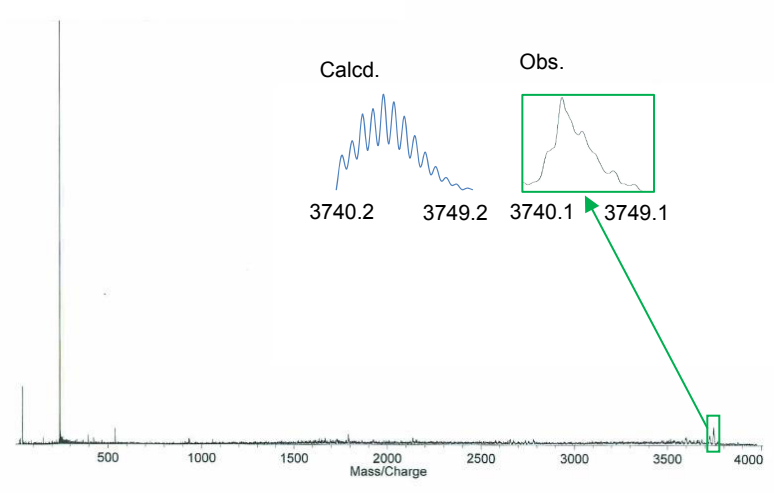
1,3-Bis(1-(dodekakistrifluoroethoxyphthalocyaninate zinc(II) yl)-1*H*-1,2,3-triazol-4-yl)benzene (**7**)



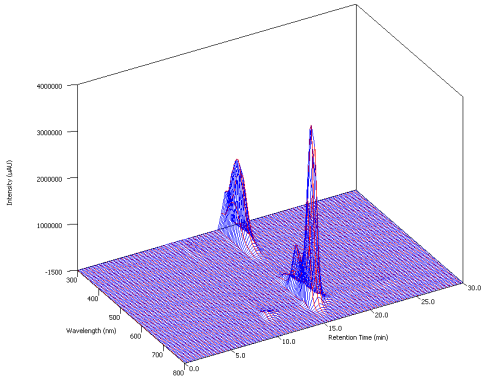
A mixture of **3** (40.0 mg, 0.0225 mmol), 1,3-bis(azidomethyl)benzene **5b** (1.7 mg, 0.009 mmol), CuI (1.0 mg, 0.005 mmol), Et_3N (0.05 ml) and DMSO (0.8 ml) was freeze dried to remove oxygen, and stirred at 60 °C for 2 h. After cooling it to rt, water and dil. sulfuric acid were added and the precipitates were filtered. Purification by silica gel column chromatography (hexane : acetone = 80: 20 to 65 : 35) gave green solids. 31.9 mg, 95%.

$C_{124}H_{64}F_{72}N_{22}O_{24}Zn_2$; M.W.: 3744.63; ^{1}H-NMR (acetone-d_6, 400 MHz): δ 5.08-5.19 (m, 24H), 5.72-5.85 (m, 24H), 5.98 (s, 4H), 7.63 (br, 3H), 7.87 (s, 1H), 8.79 (d, J = 7.2 Hz, 2H), 8.87 (s, 2H), 9.45 (d, J = 7.2 Hz, 2H), 9.82 (m, 2H); ^{19}F-NMR (acetone-d_6, 376 MHz): δ –74.1- –74.0, –73.6, –73.1, –72.8; IR (KBr): 2975, 1488, 1456, 1275, 1158, 1068, 1014, 970, 853, 761, 662 cm^{-1}; UV-vis (2.2 x 10^{-6} M in $CHCl_3$): λ_{max} (log ε) = 702 (5.70), 631 (4.97), 360 (5.19) nm; (0.5 x 10^{-6} M in $PhCF_3$): λ_{max} (log ε) = 694(5.42), 646 (4.97), 356 (5.02) nm; (0.5 x 10^{-6} M in dioxane): λ_{max} (log ε) = 702 (5.67), 632 (4.94), 359 (5.14) nm; Fluorescence ($CHCl_3$): λ_{em} = 715 nm, Φ_f = 0.26, (dioxane): λ_{em} = 715 nm, Φ_f = 0.29.

MALDI-TOF MS (dithranol): *m/z* = 3740.1-3749.1 ([M^+], isotopic pattern)



HPLC: (H_2O:MeCN:THF = 8:42:50, 0.3 ml/min), t_R = 16.1 min.



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