Electronic Supplementary Material (ESI) for Soft Matter

Electronic Supplementary Information

A soft supramolecular carrier with enhanced singlet oxygen photosensitizing properties

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Analysis

NMR spectroscopy: NMR spectra were recorded with the superconductive spectrometers ARX 300 (*Bruker*) and ARX 400 (*Bruker*) as well as Inova 500 (*Varian*) and the Unity plus 600 (*Varian*). In all measurements deuterated solvents were used. The chemical shift (δ) is recorded in parts per million (ppm). Referencing was performed using residual solvent protons or tetramethylsilane as internal standard. The measured coupling constants were recorded in Hertz (Hz). Complex spectra were analyzed using two-dimensional NMR spectroscopy. *MestReNova* 6.0.3 was used to analyze the NMR spectra. Signal description: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, b = broad.

Mass spectrometry: Mass spectra were recorded on the electrospray ionization spectrometers (ESI) Micro Tof (*Bruker Daltonics*) and on *OrbiTap LTQ-XL* (*Thermo Scientific*). High molecular mass compounds were detected using matrix assisted laser desorption ionization - time of flight (MALDI-TOF) spectrometry using *Lazarus III* (University of Münster).

IR-spectroscopy: IR spectra were recorded using a *Fourier* transformation IR spectrometer (*Type 310, Varian*). Subtraction of the background yielded the desired spectra. Vibrations were described according to their intensity (w = weak, m = medium, s = strong, br = broad). Analysis of the spectra was carried out using Resolution Pro as software.

Melting point analysis: Melting points were measured using a *Melting Point B-540* (*Büchi*) apparatus. All melting points were uncorrected. The last solvent used during the work-up is mentioned in brackets behind the temperature.

X-ray structure analysis: The X-ray data set was collected by using a *Nonius Kappa CCD* diffractometer. Programs used: data collection: *COLLECT*, data reduction: Denzo-SMN, absorption correction: Denzo stucture solution: *SHELXS-9*, stucture refinement: *SHELXL-97*, graphics *SCHAKAL* or Platon (*ORTEP*).

Preparative column chromatography and thin layer chromatography (TLC): Purification via column chromatography was carried out using silica gel with a grain size of 40-65 µm (*Merck*). Solvents for the mobile phase were used without further purification. Visualization of the collected fractions was performed using thin layer chromatography using silica coated aluminum sheets (60 F_{254}, *Merck*) with fluorescence indicator. Detected spots were visualized using UV light at 254 nm or a basic potassium permanganate solution.

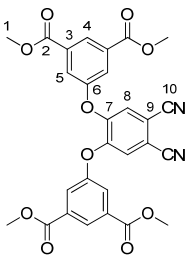
UV-Vis measurements: Absorption spectra were recorded on a double beam spectrometer (*Uvikon 923*, *Konton Instuments*, Switzerland) in low volume disposable PMMA cuvettes with a volume of 1 mL. Milli-Q water or PBS buffer (pH = 7.2) was used as solvent.

Fluorescence measurements: Fluorescence spectra were recorded on an AMINCO-Bowman Series 2 spectrometer (*Thermo Fisher Scientific Inc*., Waltham, USA) in low volume disposable PMMA cuvettes with a volume of 1 mL. Milli-Q water or PBS buffer (pH = 7.2) was used as solvent.

X-ray crystallography: Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology*, **1997**, *276*, 307-326), absorption correction SORTAV (R.H. Blessing, *Acta Cryst.* **1995**, *A51*, 33-37; R.H. Blessing, *J. Appl. Cryst.* **1997**, *30*, 421-426), structure solution SHELXS-97 (G.M. Sheldrick, *Acta Cryst.* **1990**, *A46*, 467-473), structure refinement SHELXL-97 (G.M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122), graphics XP (BrukerAXS, 2000).Graphics show the thermal ellipsoids with 50 % probability, *R* values are given for the observed reflections, wR^2 values for all reflections.

Synthesis

Tetramethyl 5,5'-((4,5-dicyano-1,2- phenylene) bis(oxy)) diisophthalate **(1)**



4,5-Dichlorophthalonitrile (1.00 g, 5.08 mmol) and dimethyl-5-hydroxyisophthalate (4.28 g, 20.36 mmol) were dissolved in 50 mL of dry DMF followed by the addition of K_2CO_3 (16.60 g, 0.12 mol). The reaction mixture was heated to 65 °C for 24 h. The crude suspension was poured into 400 mL of ice water. The precipitate was filtered and dissolved in $CHCl_3$. After washing with distilled water and brine (2 x 50 mL), the organic layer was dried over $MgSO_4$. Removal of the solvent in vacuo yielded the crude product which was further purified via column chromatography ($CHCl_3$, R_f = 0.07). Single crystals suitable for X-ray analysis were obtained by slow evaporation of a concentrated solution in $CHCl_3$.Yield: 1.99 g (3.66 mmol, 72%).Molecular formula: $C_{28}H_{20}N_2O_{10}$ (colorless solid).^{1}H-NMR (300 MHz, $CDCl_3$, 298 K): δ = 3.96 (s, 12H, 1-H), 7.32 (s, 2H, 8-H), 7.82 (d, J = 1.4 Hz, 4H, 5-H), 8.55 (t, J = 1.4 Hz, 2H, 4-H)^{13}C-NMR (300 MHz, $CDCl_3$, 298 K): δ = 52.80 (CH_3, 1-C), 112.29 (C_q, 9-C), 114.39 (CH, 4-C), 123.99 (CH, 8-C), 124.16 (CH, 5-C), 127.59 (CH, 4-C), 133.12 (C_q, 3-C), 150.77 (C_q, 7-C), 154.59 (C_q, 6-C), 164.90 (C_q, 2-C).ESI-HRMS: (m/z) Calculated for $[C_{28}H_{20}N_2O_{10}Na]^+$: 567.1011, found: 567.1010. IR (neat): ν [cm^{-1}] = 533 (m), 670 (w), 754 (m), 796 (m), 920 (w), 992 (m), 1076 (m), 1105 (m), 1220 (s), 1251 (s), 1315 (m), 1433 (m), 1505 (m), 1581 (m), 1725 (s), 2233 (w), 2956 (w).Melting point: 192-193°C ($CHCl_3$). Crystal data for $C_{28}H_{20}N_2O_{10}$ * $CHCl_3$, M = 663.83, triclinic, P1bar (No. 2), a = 9.9045(9), b = 11.4142 (10), c = 13.8121(4) Å, α = 97.031(2), β = 94.893(4), γ = 105.524(6)°, V = 1481.78(19) $Å^3$, D_c = 1.488 g cm^{-3}, μ = 3.337 mm^{-1}, *F(000)* = 680, Z = 2, λ = 1.54178 Å, T = 223(2) K, 29884 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 $Å^{-1}$, 5116 independent (R_{int} = 0.046), and 4365 observed reflections [I ≥ 2σ(I)], 401 refined parameters, R = 0.045, wR^2 = 0.117, GoF = 1.015. CCDC: 902549.

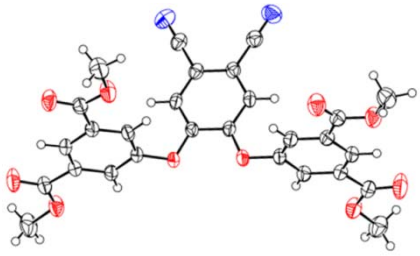
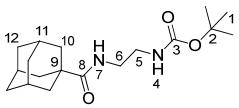


Figure S1: X-ray structure of phthalonitrile **(1)**. Thermal ellipsoids represent 50 % probability level. CCDC: 902549.

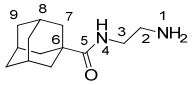
Tert-butyl(2-((3r,5r,7r)-adamantane-1-carboxamido)ethyl)-carbamate **(2)**



To a stirred solution of 1-adamantane carboxylic acid (2.70 g, 15.0 mmol) and ethyl-2-cyano-2-hydroxyiminacetate (2.66 g, 18.7 mmol) in 15 mL of DMF was added EDCI (3.59 g, 18.7 mmol). After stirring for 30 min. *tert*-butoxyethylenediamine (2.00 g, 12.5 mmol) in 3 mL of DMF was added and the reaction mixture was stirred for further 18 h. After that time the solvent was removed in vacuo and the residue was redissolved in 10 mL of CH_2Cl_2. The organic layer was washed three times with $NaHCO_3$, citric acid and

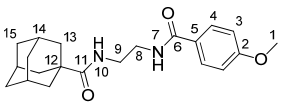
saturated NaCl solution. After removal of the solvent in vacuo the residue was purified via column chromatography ($CHCl_3$/MeOH, R_f = 0.43). Yield: 2.26 g (7.00 mmol, 56%). Molecular formula: $C_{18}H_{30}N_2O_3$ (yellow solid). ^{1}H-NMR (300 MHz, CD_2Cl_2, 298 K): δ = 1.43 (s, 9H, 1-H), 1.71-1.56 (m, 6H, 12-H), 1.82 (d, J = 2.8 Hz, 3H, 10-H), 2.01 (s, 3H, 11-H), 3.20-3.29 (m, 4H, 5,6-H), 5.22 (bs, 1H, 7-H), 6.45 (bs, 1H, 4-H). ^{13}C-NMR (300 MHz,CD_2Cl_2, 298 K): δ = 178.96 (C_q, 8-C), 157.40 (C_q, 3-C), 79.62 (C_q, 2-C), 40.82 (CH_2, 5-C), 39.54 (CH_2, 10-C), 39.22, (CH_2, 6-C), 36.90 (C_q, 9-C), 36.45 (CH_2, 12-C), 28.69 (CH_3, 1-C), 28.51 (CH_2, 11-C).ESI-HRMS: (m/z) Calculated für $[C_{18}H_{30}N_2O_3\,Na]^+$: 345.2149 found: 345.2143. IR (neat): ν [cm^{-1}] = 671 (m), 872 (w), 969 (w), 1168 (m), 1271 (m), 1364 (w), 1457 (m), 1473 (m), 1507 (m), 1522 (m), 1541 (s), 1559 (s), 1653 (m), 1685 (s), 1717 (m), 2361 (m), 2850 (m), 2903 (s), 2977 (w). Melting point: 150-150°C ($CHCl_3$).

(3s,5s,7s)-*N*-(2-aminoethyl)tricyclo[3.3.1.13,7]decan-1-carboxamide **(3)**



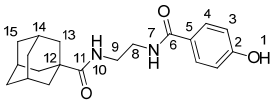
To a stirred solution of **(2)** (2.00 g, 6.19 mmol) in 10 mL of dry CH_2Cl_2 was added 1mL of trifluoroacetic acid. The solution was stirred for 6 h at room temperature followed by removal of all solvents in vacuo. The residue was purified via column chromatography (CH_2Cl_2/ MeOH/NH_4OH 9:1:0.1, R_f = 0.13). Yield: 1.11 g (5.10 mmol, 98%). Molecular formula: $C_{13}H_{22}N_2O$ (colorless solid). ^{1}H-NMR (300 MHz, DMSO-*d6*, 298 K): δ = 1.34-1.69 (m, 6H, 5-H), 1.67-1.83 (m, 6H, 7-H), 1.79-2.23 (m, 3H, 8-H), 2.58 (t, J= 6.3 Hz, 2H, 2-H), 2.97-3.05 (m, 3-H, 1,2-H), 7.29 (bs, 1H, 4-H).^{13}C-NMR (300 MHz, DMSO-*d6*, 298 K): δ = 27.62 (CH, 8-C), 36.11 (CH_2, 9-C), 40.00 (C_q, 6-C), 40.27 (CH_2, 7-C), 40.98 (CH_2, 3-C), 41.63 (CH_2, C-2), 176.99 (C_q, C-5), ESI-HRMS: (m/z) Calculated for $[C_{13}H_{22}N_2OH]^+$: 223.18; found: 223.1805. IR (neat): ν [cm^{-1}] = 637 (m), 762 (m), 795 (w), 867 (m), 908 (m), 1100 (m), 1160 (w), 1209 (m), 1280 (s), 1362 (m), 1448 (m), 1498 (m), 1537 (s), 1624 (s), 1717 (w), 2361 (w), 2849 (m), 2900 (s), 3312 (m). Melting point: 211°C ($CHCl_3$).

N-(2-((3s,5s,7s)-adamantan-1-ylamino)ethyl)-4-methoxybenzamide **(4)**



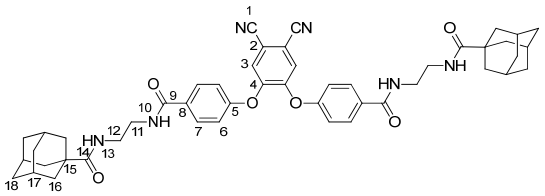
To a stirred solution of p-methoxybenzoic acid (0.34 g, 2.25 mmol) in 15 mL of DMF was added ethyl-2-cyano-2-hydroxyiminacetate (0.48 g, 3.38 mmol) and EDCI (0.72 g, 3.38 mmol). After 30 min. of stirring **(3)** (1.00 g, 2.25 mmol) in 2 mL of a 1:1 mixture of NMM and DMF was added. The clear solution was stirred overnight followed by removal of the solvents. The residue was redissolved in 50 mL of CH_2Cl_2 and washed with three times with $NaHCO_3$, citric acid and saturated NaCl solution. The organic layer was dried over $MgSO_4$ and the solvent was removed in vacuo. The obtained residue was purified via column chromatography (EtOAc, R_f = 0.32).Yield: 0.37 g (1.01 mmol, 45%). Molecular formula: $C_{21}H_{28}N_2O_3$ (colorless solid).^{1}H-NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.57-1.67 ppm (m, 6H, 15-H), 1.75 (d, J=9.0 Hz, 6H, 13-H), 1.91-1.99 (m, 3H, 14-H), 3.39-3.47 (m, 2H, 9-H), 3.46-3.54 (m, 2H, 8-H), 3.78 (s, 3H, 1-H), 6.40 (t, J = 4.8 Hz, 1H, 10-H), 6.85 (d, J= 9.0, 2H, 3-H), 7.24 (s, 1H, 7-H), 7.71 (d, J = 9.0 Hz, 2H, 4-H). ^{13}C-NMR (300 MHz, $CDCl_3$, 298 K): δ = 27.82 (CH, 14-C), 36.62 (CH_2, 15-C), 39.24 (CH_2, 13-C), 39.72 (CH_2, 9-C), 40.59 (CH_2, 8-C), 41.40 (C_q 12-C), 55.25 (CH_3 1-C), 113.50 (CH, 3-C), 126.17 (CH, 4-C), 128.88 (C_q, 5-C), 162.29 (C_q, 2-C), 168.07 (C_q, 6-C), 180.04 (C_q, 11-C). ESI-HRMS: (m/z) Calculated for $[C_{21}H_{28}N_2O_3H]^+$: 357.2173 found: 357.2175. IR (neat): ν [cm^{-1}] = 682 (m), 753 (m), 811 (w), 845 (s), 911 (w), 982 (w), 1031 (m), 1181 (s), 1251 (s), 1285 (m), 1331 (m), 1445 (m), 1510 (m), 1549 (s), 1628 (s), 2848 (w), 2902 (m), 3263 (w), 3306 (w). Melting point: 182-183°C (EtOAc).

N-(2-((3s,5s,7s)-adamantan-1-ylamino)ethyl)-4-hydroxybenzamide **(5)**



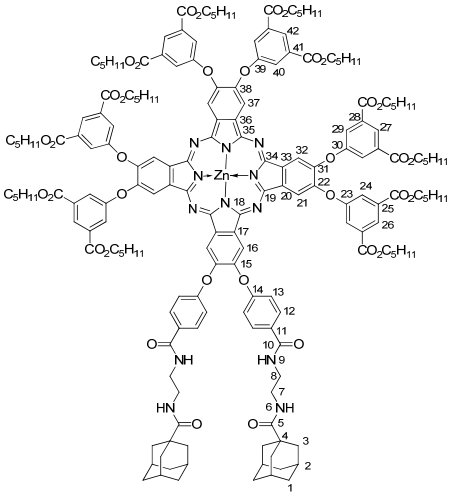
To a stirred solution of **(4)** (0.50 g, 1.75 mmol) in 30 mL of dry CH_2Cl_2 was added BBr_3 (0.33 mL, 3.5 mmol) at -78 °C. After 1 h the solution was warmed to room temperature and stirred for another 18 h. After that time the solution was diluted with 30 mL of distilled water and washed 3 times with 20 mL of brine. After drying over $MgSO_4$ and removal of the solvent the desired product was obtained. Yield: 298 mg (0.87 mmol, 50%).Molecular formula: $C_{20}H_{26}N_2O_3$ (yellow solid). ^{1}H-NMR (500 MHz, DMSO-*d6*, 298 K): δ = 1.61-1.69 (m, 6H, 15-H), 1.75 (d, *J* = 2.6 Hz, 6H, 13-H), 1.96 (s, 3H, 14-H), 3.20 (dd, *J* = 12.2 Hz, 6.3 Hz, 2H, 9-H), 3.28 (dd, 2H, *J* = 12.2 Hz, 6.3 Hz, 8-H), 6.79 (d, *J* = 8.7 Hz, 2H, 3-H), 7.49 (t, *J* = 5.4 Hz, 1H, 10-H), 7.69 (d, *J* = 8.7 Hz, 2H, 4-H), 8.22 (t, *J* = 5.5 Hz, 1H, 4-H), 9.94 (s, 1H, 1-H). ^{13}C-NMR (125 MHz, DMSO-*d6*, 298 K): δ = 27.64 (CH, 14-C), 36.16 (CH_2, 15-C), 38.70 (CH_2, 13-C), 39,82 (CH_2, 9-C), 39.12 (CH_2, 8-C), 39.78 (C_q, 12-C), 114.73 (CH, 3-C), 125.18, (C_q, 5-C), 129.03 (CH, 4-C), 160.02 (C_q, 2-C), 166.28 (C_q, 6-C), 177.28 (C_q, 11-C). ESI-HRMS: (m/z) Calculated for $[C_{20}H_{26}N_2O_3Na]^+$: 365.1836, found: 365.1874.IR (neat): ν [cm^{-1}] = 608 (w), 670 (w), 797 (s), 844 (w), 871 (w), 1022 (s), 1083 (s), 1177 (m), 1257 (s), 1366 (w), 1451 (w), 1541 (m), 1504 (m), 1631 (m), 2850 (w), 2904 (m), 3322 (w). Melting point: 153°C (CH_2Cl_2).

N,N'-(((4,4'-((4,5-dicyano-1,2-phenylene)bis(oxy))bis(benzoyl)) bis(azanediyl))bis-(ethane-2,1-diyl)) bis(adamantane-1-carboxamide) **(6)**



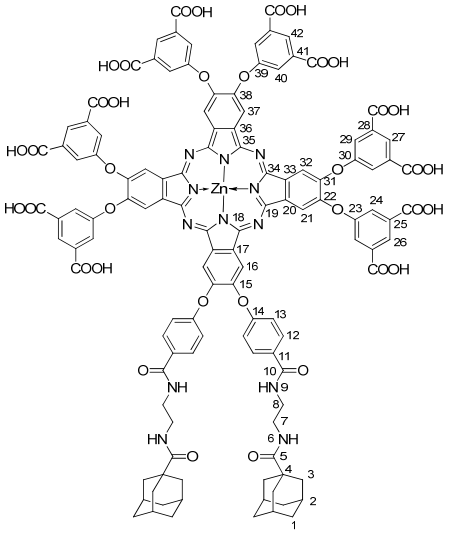
To a stirred solution of **(5)** (200 mg, 0.60 mmol) in 10 mL of DMF was added 4,5-dichloro-phthalonitrile (52.1 mg, 0.27 mmol) followed by powdered K_2CO_3 (16.2 mmol, 2.22 g). The mixture was heated to 65°C for 24 h. After that time the solvent was evaporated and the residue was dissolved in 20 mL $CHCl_3$, and washed three times with 10 mL of water. The combined organic layers were dried over $MgSO_4$ and the solvent was removed in vacuo. The crude product was further purified by column chromatography ($CHCl_3$/MeOH 9:1, R_f = 0.83). Yield: 233 mg, Molecular formula: $C_{48}H_{52}N_6O_6$ (colorless solid). ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.67 (q, *J* = 12.2 Hz, 12H, 18-H), 1.80 (d, *J* = 2.4 Hz, 12H, 16-H), 1.99 (bs, 6H, 17-H), 3.46-3.59 (m, 8H, 11,12-H), 6.55 (t, *J* = 5.2 Hz, 2H, 13-H), 7.02 (d, *J* = 8.8 Hz, 4H, 7-H), 7.30 (s, 2H, 3-H), 7.85 (t, *J* = 5.2 Hz, 2H, 10-H), 7.90 (d, *J* = 8.8 Hz, 4H, 6-H). ^{13}C-NMR (75.5 MHz, $CDCl_3$, 298 K): δ = 27.98 (CH, 17-C), 36.38 (CH_2, 18-C), 39.11 (CH_2, 16-C), 39.52 (CH_2, 12-C), 40.61 (CH_2, 11-C), 41.89 (C_q, 15-C), 111.59 (Cq, 2-C), 114.61 (Cq, 1-C), 118.86 (CH, 6-C), 123.85 (CH, 3-C), 129.72 (CH, 7-C), 131.32 (Cq, 8-C), 151.08 (Cq, 4-C), 156.79 (C_q, 5-C), 166.81 (C_q, 9-C), 180.47 (C_q, 14-C). ESI-HRMS: (m/z) Calculated for $[C_{48}H_{52}N_6O_6Na]^+$: 831.3841, found: 831.3830. IR (neat): ν [cm^{-1}] = 663 (w), 673 (m), 766 (w), 825 (w), 872 (m), 901 (m), 1026 (w), 1075 (w), 1098 (w), 1231 (s), 1283 (s), 1332 (w), 1398 (w), 1497 (s), 1541 (m), 1587 (m), 1630 (s), 2850 (w), 2904 (br), 3304 (br). Melting point: 233°C ($CHCl_3$).

Zinc(II) 2,3,9,10,16,17,-dodecyl(3,5-bispentyloxycarbonyl) phenoxy-23,24-bisadamantyl-phthalocyanine **(7)**



A mixture of **(5)** (200 mg, 0.24 mmol), **(1)** (539 mg, 0.96 mmol), $Zn(OAc)_2$ x $2H_2O$ (242 mg, 0.44 mmol) and 2 drops of DBU were dissolved in 10 mL of *n*-pentanol and heated overnight to 140°C. All volatiles were removed in vacuo and the blue residue was purified via column chromatography ($CHCl_3$). The first blue fraction contains exclusively the symmetrical product. The second blue fraction contains the desired unsymmetrical product, which was further purified by semipreparative HPLC (THF / cyclohexane 1:1→ 1:0). Yield: 21 mg (0.0069 mmol, 2.9 %). Molecular formula: $C_{180}H_{208}N_2O_{36}Zn$ (dark blue solid). ^{1}H-NMR (600 MHz, $CDCl_3$, 298 K): δ = 0.73 (t, *J* = 7.1 Hz, 18H, 6 CH_3), 0.82 (t, *J* = 7.1 Hz, 12H, 3 CH_3), 0.87 (t, *J* = 7.1 Hz, 12H, 3 CH_3), 0.97-1.60 (m, 96 H, 48 CH_2), 1.61-1.68 (m, 12H, 1-H), 1.81 (d, *J* = 2.4 Hz, 12H, 3-H), 1.97 (s, 6H, 2-H), 3.45-3.59 (m, 8H, 7,8-H), 5.23-5.25 (m, 4H), 6.73 (t, *J* = 6.3 Hz, 2H, 6-H), 6.75 – 6.70 (m, 2H), 7.20 (d, *J* = 8.8 Hz, 4H, 12-H), 7.58, 7.92, 7.97 (3d, *J* = 1.1 Hz, 12H, 24,29,40-H), 7.67 (bs, 2H, 9-H), 7.92 (s, 4H), 7.97 (s, 4H), 7.99 (d, *J* = 8.9 Hz, 4H, 13-H), 8.09, 8.44, 8.47 (3s, 6H, 26,27,42-H), 8.50 (s, 2H), 8.79, 9.17, 9.22, 9.27, 9.33, 9.37, 9.92, 10.23 (8s, 8H, 16,21,32,37). ^{13}C-NMR (126 MHz, $CDCl_3$, 298 K): δ 13.79, 13.87, 13.88, 13.92, 13.95, (12 CH_3) 22.13, 22.24, 22.26, 22.30, 22.33 (12 CH_2), 27.89 (CH, 2-C), 27.76, 27.80, 27.87, 28.05, 28.07, 28.12, 28.26, 28.30, 28.31, 28.33 (24 CH_2) 36.23, 36.46 (CH_2, 1-H), 38.78, 39.13 (CH_2, 3-H), 64.86, 65.42, 65.62, 65.69, 65.79, 65.81 (12 CH_2) 115.24, 115.44, 115.53, 116.04, 116.60, 116.71, 116.81, 117.05, 117.15 (CH, 16,21,32,37-C), 118.91 (CH), 119.79 (CH), 121.03 (CH), 121.97 (CH), 122.11 (CH), 122.22 (CH), 122.35 (CH), 122.83 (CH), 123.14 (CH), 125.13 (CH), 125.37 (CH), 125.51 (CH), 126.34 (CH), 126.95 (CH), 127.50 (CH), 127.96 (CH), 128.13 (CH), 129.08 (CH), 129.48 (CH), 129.73 (CH), 131.40 (C_q), 132.22 (C_q), 132.50 (C_q), 132.61 (C_q), 132.72 (C_q), 133.05 (C_q), 133.68 (C_q), 135.36 (C_q), 135.54 (C_q), 135.68 (C_q), 136.20 (C_q), 136.27 (C_q), 136.35 (C_q), 136.41 (C_q), 136.44 (C_q), 136.50 (C_q), 136.53 (C_q), 136.56 (C_q), 136.66 (C_q), 136.71 (C_q), 139.48 (C_q), 145.26 (C_q), 145.61 (C_q), 145.83 (C_q), 146.24 (C_q), 48.11 (C_q), 148.19 (C_q), 148.25 (C_q), 148.32 (C_q), 148.58 (C_q), 148.75 (C_q), 149.05 (C_q), 149.24 (C_q), 149.49 (C_q), 151.00 (C_q), 151.68 (C_q), 151.84 (C_q), 151.92 (C_q), 152.06 (C_q), 152.17 (C_q), 152.45 (C_q), 152.64 (C_q), 152.73 (C_q), 153.03 (C_q), 153.08 (C_q), 153.14 (C_q), 153.27 (C_q), 153.38 (C_q), 154.77 (C_q), 155.64 (C_q), 156.22 (C_q), 156.89, 157.10, 157.20, 157.57, 157.69, 157.79 (C_q, 14,23,30,39-C) 158.11 (C_q), 158.24 (C_q), 158.33 (C_q), 159.49 (C_q), 161.30 (C_q), 161.88 (C_q), 162.58 (C_q), 164.12, 164.77, 164.87, 165.20, 165.23, 165.28, 165.33, 166.34, 167.10, 167.34, 167.48 (12C_q, $CO_2C_5H_{11}$) , 175.45, 179.72, 180.56, 181.27 (C_q, 14-C). MALDI-MS (m/z): Calculated for $[C_{180}H_{208}N_2O_{36}ZnH]^+$: 3178.4, found: 3178.9. IR (neat): ν [cm^{-1}] = 668 (w), 717 (w), 756 (s), 828 (w), 912 (w), 978 (m), 1034 (m), 1101 (m), 1169 (m), 1230 (s), 1309 (s), 1359 (w), 1392 (w), 1453 (m), 1593 (m), 1721 (s), 2872 (w), 1933 (w), 2957 (w), 3278 (br). Melting point: 151°C (THF).

Zinc(II) 2,3,9,10,16,17,-dodecyl(3,5-biscarboxylate)phenoxy-23,24-bisadamantyl- phthalocyanine **(8)**



Compound **(7)** (21 mg, 0.0069 mmol) was dissolved in 2 mL of THF followed by the addition of saturated NaOH solution in water/methanol (1:5) (10 mL). The mixture was stirred for 4 h at room temperature. The resulting precipitate was collected by decanting the supernatant. The greenish powder was dissolved in 2 mL of water and acidified using 1 M HCl to pH 2. The obtained solid was collected by filtration and dried in vacuo. Yield: 14 mg (0.0060 mmol, 87 %). Molecular formula: $C_{120}H_{88}N_{12}O_{36}Zn$ (green solid). MALDI-MS (m/z): Calculated for $[C_{132}H_{112}N_{12}O_{36}ZnNa]^{+\cdot}$ 2528 found: 2528. IR (neat): ν [cm^{-1}] = 673 (w), 711 (w), 766 (w), 891 (w), 972 (m), 1031 (s), 1087 (s), 1170 (m), 1217 (w), 1268 (s), 1394 (s), 1448 (m), 1490 (w), 1567 (m), 1606 (w), 1705 (w), 2907 (br), 3351 (br). Melting point: 286°C (H_2O) decomposition.

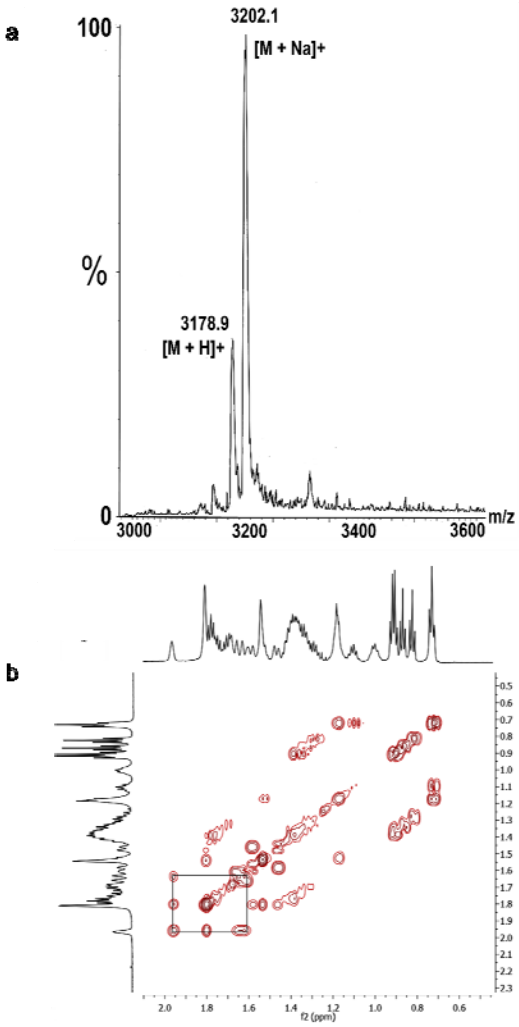


Figure S2: a) Maldi-MS spectrum of compound **(7)** and b) 2D-NMR ^{1}H-^{1}H correlation of compound **(7)**, the square shows the adamantane spin system.

Dynamic light scattering

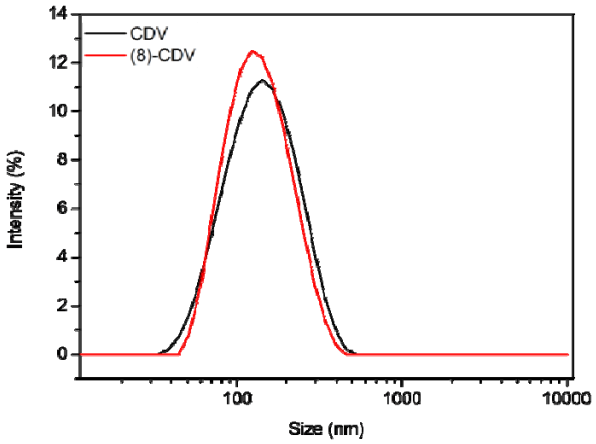


Figure S3: Size distribution of cyclodextrin vesicles (CDV) and cyclodextrin vesicles decorated with phthalocyanine (**8**-CDV) measured by dynamic light scattering.

Determination of singlet molecular oxygen quantum yields

Singlet molecular oxygen photogeneration rates were derived using photochemical monitor bleaching rates. Polychromatic irradiation by a projector lamp (Leica ZETT Royal II afs) that passed through a cut-off filter at 610 nm was applied to perform the experiments. Calculation of the singlet oxygen quantum yield for the ZnPc-Vesicles was done according to eqn. S1, where r is the singlet oxygen photogeneration rate (measured as slope of the monitor's bleaching over time), λ_1 - λ_2 is the irradiation wavelength interval, $I_o(\lambda)$ the incident spectral photon flow, $A(\lambda)$ the absorbance, and the subscripts R and S stand for reference (MB) and sample (**(8)** or **(8)**-CDV), respectively.

$$\phi_{\Delta}^{S} = \phi_{\Delta}^{R} \frac{r_S}{r_R} \frac{\int_{\lambda_1}^{\lambda_2} I_0(\lambda)\left(1-10^{-A_R(\lambda)}\right) d\lambda}{\int_{\lambda_1}^{\lambda_2} I_0(\lambda)\left(1-10^{-A_S(\lambda)}\right) d\lambda} \qquad \text{(eqn. S1)}$$

The incident intensity can be approximated by a constant value, drawn out of the integral and therefore cancelled. The measured data is depicted in Figure S4, where the bleaching of the monitor is shown for the reference, and for the free phthalocyanine or the decorated vesicles.

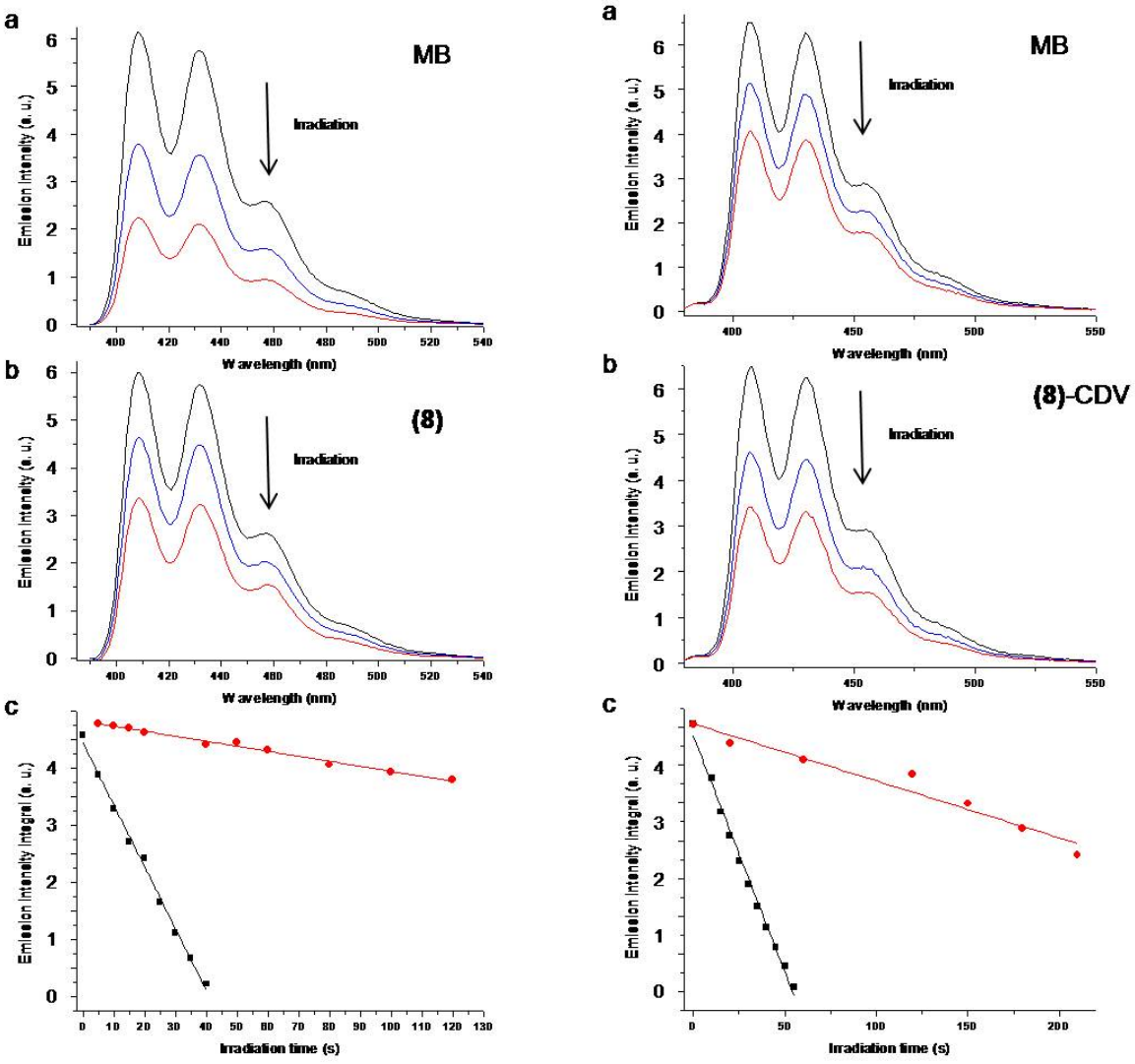


Figure S4: Emission spectra of ADMADM at different irradiation times with: a-left) MB (0 s, 60 s and 120 s); b-left) **(8)** (0 s, 1140 s, 3240 s); a-right) MB (0 s, 25 s and 50 s); b-right) **(8)**-CDV (0 s, 240 s, 480 s). c) Decay of ADMADM for **(8)** (left, red line) or **(8)**-CDV (right, red line) and for MB (left and right, black line).

Fluorescence quantum yields

All experiments were performed at room temperature. Absorption, fluorescence excitation and emission spectra of **(8)** and **(8)**-CDV in air saturated H_2O were recorded at comparable concentrations by using a 10 x 10 mm quartz cuvette for fluorescence spectroscopy. Relative fluorescence quantum yields (Φ_F) were determined by comparison with tetra-*t*-butylphthalocyanatophthalocyaninato zinc(II) (Φ_F = 0.30 in toluene) as a reference. The calculation of the quantum yields was carried out using eqn. S2, where *I* is the integral of the emission spectrum, *A* is the absorbance of the solution at the excitation wavelength, $(n_S/n_R)^2$ is the refractive index correction and *R* and *S* refer to the reference and sample, respectively.

$$\phi_F^S = \phi_F^R \frac{r_S}{r_R} \frac{I_S\,(1-10^{-A_R})}{I_R\,(1-10^{A_S})} \left(\frac{n_S}{n_R}\right)^2 \qquad \text{(eqn. S2)}$$