Supplementary data

General. All solvents were SLR or analytical grade and were used as supplied or after drying. Infrared spectra were recorded neat on a Perkin Elmer Spectrum BX equipped with a DuraSamplIR II ATR attachment. NMR spectra were recorded at 400 MHz for ^{1}H and 75.4 MHz for ^{13}C on a Varian Unity plus spectrometer. UV-vis spectra were recorded using a Perkin Elmer Lambda 35 spectrophotometer and fluorescence spectra were obtained from a Fluoromax 2 fluorimeter (ISA Instruments S.A., Inc.) Maldi-tof mass spectra were obtained using either an Applied Biosystems Vogager-DE-STR instrument at the EPSRC National Spectrometry Service Centre, Swansea, with DCTB (trans-2-[3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile) as matrix, or as neat samples using an in-house Kratos Analytical Axima-CFR instrument.

Materials Chlorosubphthalocyanine **8** was purchased from Aldrich. 1,4,8,11,15,18,22,25-octakis(hexyl)-dihydroxysilicon phthalocyanine[12] **1** was prepared by literature procedures. Dihydroxysilicon octaethylporphyrin[13] **2** and dihydroxygermanium octaethylporphyrin[14] **4** were prepared by adaptations of reported routes to these compounds.

Phthalocyanine/porphyrin heterodyads

Dyad ***5:***- The germanium porphyrin **4** (43.6 mg, 0.035 mmol) and the silicon phthalocyanine **1** (43.6mg, 0.035 mmol) were placed in a sealed tube (20 ml capacity). Dry pyridine (5ml) was added under nitrogen. The tube was sealed and heated to 160° for 14h. After cooling to rt, DCM (30ml) was added and the organic phase was washed with a 2% solution of hydrochloric acid (3×100 ml), water (3×100 ml) and brine (3×100 ml). After removal of the solvent, the solid was dissolved in a minimum volume of DCM and chromatographed over basic Al_2O_3. The first band, unreacted **1,** was eluted with toluene and the second band (blackish-blue) was eluted using DCM. Removal of solvent afforded the blackish-blue *phthalocyanine-porphyrin dyad* ***5*** (15.1 mg, 23%) which was recrystallized from CH_2Cl_2/acetonitrile. R_f 0.27 (Al_2O_3, DCM); δ_H (400 MHz, C_6D_6) 9.36 (4H, s, $H_{meso\text{-}GeOEP}$), 8.15 (8H, s, H_{arom}), 5.16-5.23 (8H, m, Ar-CH-), 4.64-4.71 (8H, m, Ar-CH-), 4.16-4.14 (8H, m, Pyrrole-CH-), 3.58-3.65 (8H, m, $H_{Pyrrole\text{-}CH\text{-}}$), 2.49-2.57 (16H, m, $H_{aliphatic}$), 2.00-2.07 (16H, m, $H_{aliphatic}$), 1.51-1.68 (56H, m, $H_{aliphatic+OEP\text{-}CH3}$), 1.02-1.06 (24H, t, *J* 7.32 CH_3-); δ_H (400 MHz, CD_2Cl_2) 8.96 (4H, s, $H_{meso\text{-}GeOEP}$), 8.10 (8H, s, H_{arom}), 4.84-4.90 (8H, m, Ar-CH-), 4.33-4.40 (8H, m, Ar-CH-), 3.75-3.81 (8H, m, Pyrrole-CH-), 3.86-3.44 (8H, m, $H_{Pyrrole\text{-}CH\text{-}}$), 2.24-2.37 (16H, m, $H_{aliphatic}$), 1.74-1.81 (16H, m, $H_{aliphatic}$), 1.42-1.53 (56H, m, $H_{aliphatic+OEP\text{-}CH3}$), 0.88-0.93 (24H, t, *J* 7.22 CH_3-); δ_C (75 MHz, CD_2Cl_2) 146.6, 140.3, 140.0, 137.8, 132.7, 129.6, 93.7 (OEP), 32.5, 32.4, 29.3, 29.1, 22.6, 19.0 (OEP), 17.8 (OEP), 13.7; MALDI-MS: isotopic clusters at 1869.8 M^+ and 1852.8 M^+-OH; λ_{max} (logε/M^{-1}•cm^{-1}) (Toluene) 746(4.67), 669(4.11), 605(4.26), 561(4.08), 484(4.25), 408(5.03), 338nm (4.81).

Dyad ***6:***- A solution of the heterodyad **5** (6.2 mg, 0.0033 mmol) in DCM (5 ml) was cooled to 0°. A solution of boron trifluoride-diethyl ether complex (1 ml of a prepared 1×10^{-2} M solution in DCM, 0.01 mmol) was added to the blackish blue solution which instantaneously turned black green. The reaction solution was stirred for 10 min at 0°. DCM (30 ml) was added to the resulting blackish blue solution and the organic layer was

washed with water (50 ml), 1% aqueous sodium hydroxide (20 ml), water (3×100 ml) and brine (3×100 ml). After concentration under reduced pressure, the blackish blue *difluoro dyad* ***6*** was recovered (6.2mg, 95%) and recrystallized from CH_2Cl_2/acetonitrile. R_f 0.31 (Al_2O_3, DCM); δ_H (400 MHz, C_6D_6) 9.36 (4H, s, $H_{meso\text{-}GeOEP}$), 8.14 (8H, s, H_{arom}), 5.10-5.18 (8H, m, Ar-CH-), 4.60-4.67 (8H, m, Ar-CH-), 4.01-4.11 (8H, m, Pyrrole-CH-), 3.55-3.61 (8H, m, $H_{Pyrrole\text{-}CH\text{-}}$), 2.44-2.53 (16H, m, $H_{aliphatic}$), 1.97-2.04 (16H, m, $H_{aliphatic}$), 1.54-1.67 (56H, m, $H_{aliphatic+OEP\text{-}CH3}$), 1.03-1.07 (24H, t, *J* 7.56 CH_3-);
δ_H (400 MHz, CD_2Cl_2) 8.97 (4H, s, $H_{meso\text{-}GeOEP}$), 8.12 (8H, s, H_{arom}), 4.85-4.90 (8H, m, Ar-CH-), 4.32-4.39 (8H, m, Ar-CH-), 3.74-3.80 (8H, m, Pyrrole-CH-), 3.38-3.44 (8H, m, $H_{Pyrrole\text{-}CH\text{-}}$), 2.22-2.36 (16H, m, $H_{aliphatic}$), 1.73-1.81 (16H, m, $H_{aliphatic}$), 1.45-1.53 (56H, m, $H_{aliphatic+OEP\text{-}CH3}$), 0.89-0.93 (24H, t, *J* 7.51 CH_3-); δ_C (75 MHz, CD_2Cl_2) 146.9, 141.1, 140.2, 140.1, 138.0, 132.6, 129.7, 93.7 (OEP), 32.5, 32.4, 30.0, 29.1, 22.6, 19.0 (OEP), 17.8 (OEP), 13.7; δ_F (CD_2Cl_2) -95.52 (F-SiPc), -101.45 (F-GeOEP); MALDI-MS: isotopic clusters at 1873.6 M^+ and 1854.6 M^+-OH; λ_{max} (logε/M^{-1}•cm^{-1}) (Toluene) 741(4.66), 663(4.10), 603(4.11), 557(3.95), 483(4.04), 404(5.02), 341nm(4.58).

Dyad 7:- To a solution of the dihydroxy dyad **5** (18.7 mg, 0.01 mmol) in pyridine (5 ml) was added t-butyldimethylsilylchloride, TBDMSCl, (23.7 mg, 0.15 mmol) and the solution stirred for 4 h at rt the in dark. DCM (20 ml) was added and the organic layer was successively washed with 2% HCl aqueous (2×50 ml), a 2% aqueous sodium hydroxide (20 ml), and water (3×100 ml). After removal of solvent the dark blue residue was chromatographed over basic aluminium oxide (DCM as eluent) to afford the *mono-TBDMS derivatized dyad* ***7*** (17.2 mg, 87%) which was recrystallized from CH_2Cl_2/acetonitrile. R_f 0.33 (Al_2O_3, DCM); δ_H (400 MHz, C_6D_6) 9.35 (4H, s, $H_{meso\text{-}GeOEP}$), 8.16 (8H, s, H_{arom}), 5.33-5.37 (8H, m, Ar-CH-), 4.60-4.64 (8H, m, Ar-CH-), 4.01-4.15 (8H, m, Pyrrole-CH-), 3.60-3.66 (8H, m, $H_{Pyrrole\text{-}CH\text{-}}$), 2.52-2.56 (16H, m, $H_{aliphatic}$), 1.91-1.96 (16H, m, $H_{aliphatic}$), 1.43-1.62 (56H, m, $H_{aliphatic+OEP\text{-}CH3}$), 0.94-0.99 (24H, t, *J* 7.49 CH_3-), -2.03 (9h, s, t-butylSiPc), -3.70 (6h, s, t-butylSiPc); δ_H (400 MHz, CD_2Cl_2) 8.97 (4H, s, $H_{meso\text{-}GeOEP}$), 8.09 (8H, s, H_{arom}), 4.93-5.01 (8H, m, Ar-CH-), 4.27-4.31 (8H, m, Ar-CH-), 3.78-3.83 (8H, m, Pyrrole-CH-), 3.40-3.47 (8H, m, $H_{Pyrrole\text{-}CH\text{-}}$), 2.19-2.34 (16H, m, $H_{aliphatic}$), 1.64-1.70 (16H, m, $H_{aliphatic}$), 1.28-1.48 (56H, m, $H_{aliphatic+OEP\text{-}CH3}$), 0.80-0.86 (24H, t, *J* 7.37 CH_3-); -2.44 (9h, s, t-butylSiPc), -4.23 (6h, s, t-butylSiPc); δ_C (75 MHz, CD_2Cl_2) 146.5, 140.4, 140.0, 137.8, 132.8, 129.5, 93.7 (OEP), 32.5, 32.3, 30.1, 28.8, 22.5, 22.1 (tert-Bu) 19.0 (OEP), 17.8 (OEP), 13.6, -8.9 (Si-Me); MALDI-MS: isotopic clusters at 1984.0 M^+ and 1866.9 M^+-OH; λ_{max} (logε/M^{-1}•cm^{-1}) (Toluene) 747(4.55), 670(4.11), 605(4.35), 561(4.11), 483(4.29), 407(5.03), 338nm (4.72).

μ-Oxo-linked Sub/Pc and SubPc/Pc/SubPc arrays

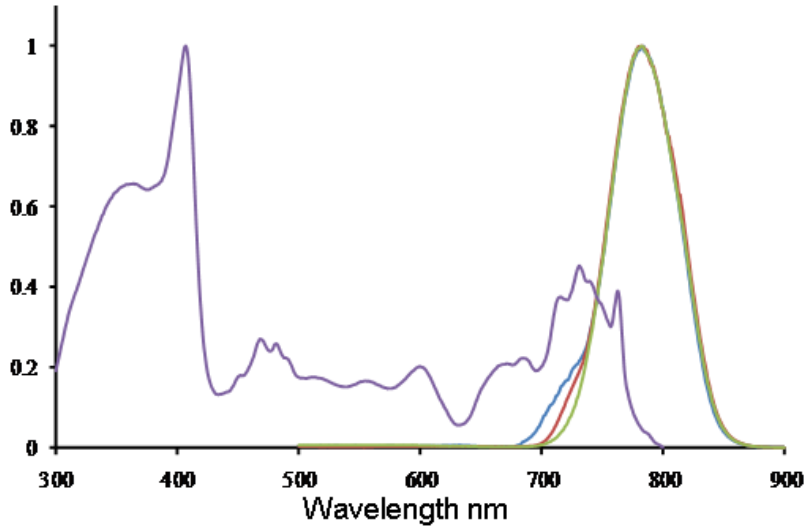
Dyad ***9*** *and triad* ***10:-*** A solution of chlorosubphthalocyanine **2** (86.1 mg, 0.2 mmol) and the silicon phthalocyanine **1** (124.8 mg, 0.1 mmol) in dry pyridine (10 ml) under nitrogen was heated to 130° in a sealed tube (30 ml capacity) for 8h. After cooling to rt, a second portion of **2** (86.1 mg, 0.2 mmol) was added, and the reaction continued, again under nitrogen, for a further16 h. When cold, pyridine was removed under vacuum. The residue was dissolved in a minimum volume of DCM and separated over basic Al_2O_3. The first green band, unreacted **1**, was eluted with toluene/cyclohexane (1/1.5). A blue-purple band, triad **10** (2.6 mg, 1.3 %), was eluted with toluene/cyclohexane (1.5/1) and this was followed by a second blue-purple band, diad **9** (21.7 mg, 13.2%), that was eluted on

changing the eluent to toluene/cyclohexane (2/1). Compounds **9** and **10** recrystallized from CH_2Cl_2/acetonitrile.

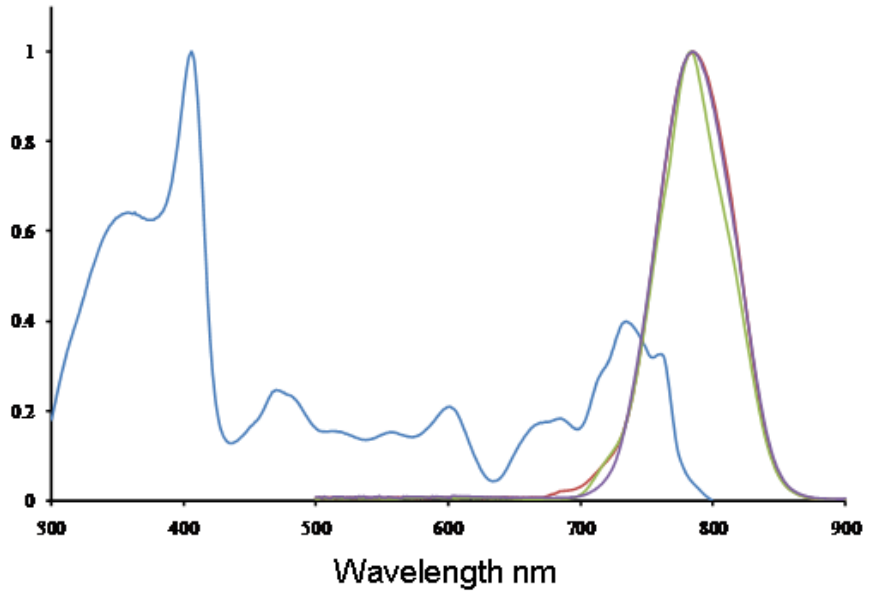
Dyad ***9***: δ_H (400 MHz, CD_2Cl_2) 7.96 (6H, m, SubPc-1, 4-H_{arom}), 7.84 (8 h, s, Pc-2, 3-H_{arom}), 7.44 (6H, m, SubPc-2, 3-H_{arom}), 4.41 (8H, m, Ar-CH-), 4.14 (8H, m, Ar-CH-), 2.13 (16H, m, $H_{aliphatic}$), 1.62 (16H, m, $H_{aliphatic}$), 1.41 (32H, m, $H_{aliphatic}$), 0.86 (24H, t, *J* 7.2, $H_{aliphatic}$-CH_3); δ_C (300 MHz, CD_2Cl_2) 148.0, 146.9, 138.7, 133.3, 130.1, 129.1, 127.8, 120.1, 31.8, 31.7, 29.7, 28.6, 22.2, 13.3. MALDI-MS: isotopic clusters at 1641.70 M^+ and 1624.67 M^+-OH. λ_{max} abs (logε/M^{-1}•cm^{-1}) (Toluene) 728(4.94), 652(4.35), 560(4.62), 373(4.54).

Triad ***10***: δ_H (400 MHz, CD_2Cl_2) 7.82 (12H, m, SubPc-1, 4-H_{arom}), 7.72 (8 h, s, Pc-2, 3-H_{arom}), 7.34 (12H, m, SubPc-2, 3-H_{arom}), 4.10 (16H, t, Ar-CH-), 2.15 (16H, m, $H_{aliphatic}$), 1.62 (16H, m, $H_{aliphatic}$), 1.41 (32H, m, $H_{aliphatic}$), 1.03 (24H, t, *J* 7.2, $H_{aliphatic}$-CH_3).MALDI-MS: isotopic clusters at 2036.08 M^+; λ_{max} abs (logε/M^{-1}•cm^{-1}) (Toluene) 735(4.91), 657(4.35), 558(4.90), 373(4.81).

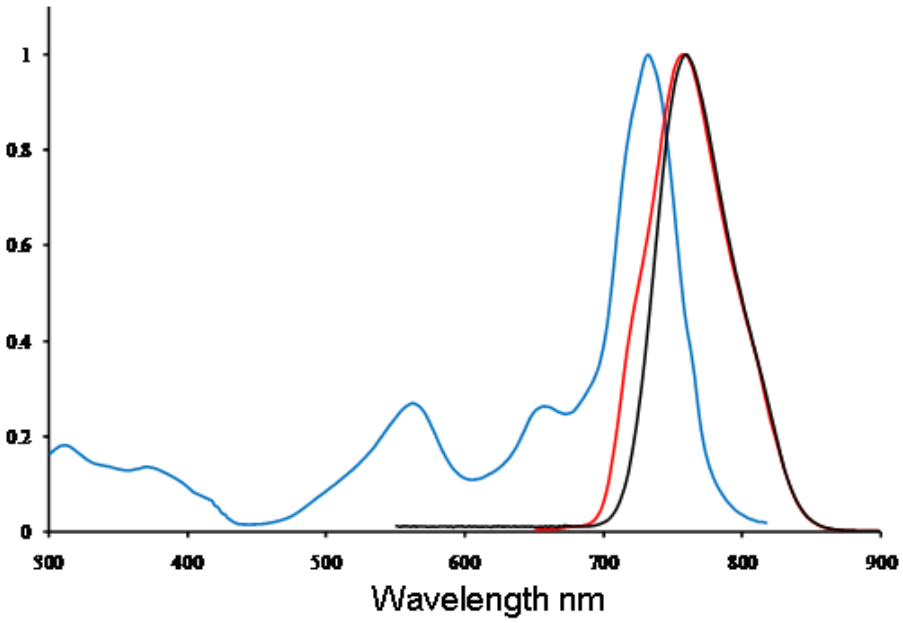
Spectra



Fluorescence spectrum of compound **5** as a solution in toluene (ca 1×10^{-6} M) measured using excitation at 345nm (blue line), 395nm (red line), 460nm (green line) nm. Emission max occurs at 784 nm. Excitation using 595 and 670 nm irradiation gave the same spectra. The excitation spectrum (815nm) is shown in purple. Vertical scale corresponds to relative normalised emissions and absorptions.



Fluorescence spectrum of compound **7** as a solution in toluene (ca 1×10^{-6} M) measured using excitation at 345nm (red line), 395nm (green line), 460nm (purple line) nm. Emission max occurs at 784 nm. Excitation using 595 and 670 nm irradiation gave the same spectra. The excitation spectrum (815nm) is shown in blue. Vertical scale corresponds to relative normalised emissions and absorptions.



Fluorescence emission spectra of diad **9** in toluene (conc. ca. 1×10^{-6} M) using excitation at 520nm (black line), and 620nm (red line). The blue line shows the excitation spectrum using an excitation wavelength of 830nm. Vertical scale corresponds to relative normalised emissions and absorptions.