Electronic Supplementary Information for:

Synthesis of Water Soluble PEGylated (Copper) Phthalocyanines via Mitsunobu Reaction and Cu(I)-catalysed Azide-Alkyne Cycloaddition (CuAAC) "Click" Chemistry

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5,6-Dichloro-1,3-isobenzofurandione (2)

A suspension of 4,5-dichlorophthalic acid (23.5 g, 0.1 mol) and Ac_2O (50 mL) was heated to slow reflux for 5 hours which allowed for the removal of AcOH by a slow distillation. After cooling, the precipitate was isolated by filtration and washed intensively with petroleum ether (bp 40-60 ^oC). The white product was dried under vacuum (Yield: 70%). ^1H NMR (400.03 MHz, $CDCl_3$, 298 K): δ 8.11 (s, 2H); ^{13}C NMR (100.59 MHz, $CDCl_3$, 298 K): δ 160.65, 141.69, 130.25, and 127.41. IR (neat): ν = 1860, 1830, 1775 (C=O, anhydride), 1100 (C-O), 730, 715, 606 cm^{-1}. ESI-MS m/z: calcd for $C_8H_2Cl_2O_3$ 216.94 $[M+H]^+$, observed 217.00.

5,6-Dichloro-1*H*-isoindole-1,3(2*H*)-dione (3)

Compound **2** (14.88 g, 0.069 mol) was heated under stirring in $HCONH_2$ (27 mL) for 3 hours under reflux. After cooling, the precipitate was isolated by filtration, washed with distilled water and dried in vacuum oven (60 ^oC) (Yield: 93%). ^1H NMR (400.03 MHz, $CDCl_3$+DMSO, 298 K): δ 10.71 (br, 1H imide), 7.80 (s, 2H); ^{13}C NMR (100.59 MHz, $CDCl_3$+DMSO, 298 K): δ 167.01, 138.41, 132.00, and 125.03. IR (neat): ν = 1770, 1718 (imide), 740, 701, 600 cm^{-1}.

4,5-Dichloro-1,2-benzenedicarboxamide (4)

Compound **3** (13.85 g, 0.064 mol) was stirred for 24 hours in 35% NH_4OH (300 mL); A further 100 mL NH_4OH was added and stirred continuously for 24 hours. The precipitate was isolated by filtration, washed with ice water and dried at 60 ^oC in a vacuum oven (Yield: 78%). ^1H NMR (400.03 MHz, DMSO-d_6, 298 K): δ 7.92 (s, 2H, NH_2), 7.75 (s, 2H), 7.54 (s, 2H, NH_2); ^{13}C NMR (100.59 MHz, DMSO-d_6, 298 K): δ 167.66, 136.6, 131.63, and 129.61. IR (neat): ν = 3430, 3303, 3142 (N-H), 1687, 1656, 1609 (C=O, amide) cm^{-1}. ESI-MS m/z: calcd for $C_8H_6Cl_2N_2O_2$ 254.97 $[M+Na]^+$, observed 254.90.

4,5-Dichloro-1,2-dicyanobenzene (5)

$SOCl_2$ (16 mL) was added dropwise to dry DMF (25 mL) at 0 ^oC under stirring and an atmosphere of nitrogen. After complete addition of $SOCl_2$, the solution was stirred at 0 ^oC for 2 hrs, followed by addition of dry compound **4** (4.66 g, 0.02 mol). The mixture was stirred for 5 hrs at 0-5 ^oC, and then at ambient temperature overnight. The mixture was added to ice water. After filtration, the crude product was recrystallised from MeOH and dried in vacuum to give dark orange crystals (Yield: 59%). ^1H NMR (400.03 MHz, $CDCl_3$, 298 K): δ 7.91 (s, 2H); ^{13}C NMR (100.59 MHz, $CDCl_3$, 298 K): δ 139.05 (2 x *C*Cl), 134.94 (2 x *C*H), 115.03 (2 x *C*CN), and 113.60 (2 x *C*N). IR (neat): ν = 3086, 3016 (C-H), 2238 (CN), 732, 684 cm^{-1}. ESI-MS m/z: calcd for $C_8H_2Cl_2N_2$ 197.95 $[M+H]^+$, observed 197.0.

4,5-Bis(4-hydroxyphenoxy)phthalonitrile (6)

A mixture of hydroquinone (3.30 g 0.03 mol), dry fine powder K_2CO_3 (13.8 g 0.1 mol), and dry DMSO (75 mL) was stirred at ambient temperature under nitrogen for 30 min. Compound **5** (1.97 g 0.01 mol) was then added and the reaction mixture was maintained at 90 ^oC with stirring for 12 h. After cooling to ambient temperature, the reaction mixture was poured into 1M HCl (250 mL) to induce precipitation. The precipitate was then filtered, washed with cold water, and redissolved in ethyl acetate. The resulting solution was washed with distilled water (3 x 100 mL) until the aqueous phase became neutral, dried with anhydrous $MgSO_4$, and the solvent removed under reduced pressure to obtain light tan colour solid. The solid was then powdered, and dispersed in CH_2Cl_2 (400 mL) with vigorous stirring. The precipitate was filtered to obtain the pure product (Yield: 74%). ^1H NMR (400.03 MHz , DMSO-d_6, 298 K): δ 9.58 (s, 2H), 7.48 (s, 2H), 7.05-7.01 (m, 4H), 6.84-6.88 (m, 4H); ^{13}C NMR (100.59 MHz , DMSO-d_6, 298 K): δ 154.89, 151.97, 146.19, 122.01, 120.81, 116.57, 115.51 (2 x *C*CN), and 109.36 (2 x *C*N). IR (neat): ν = 3400 (O-H), 2238 (CN) cm^{-1}. ESI-MS m/z: calcd for $C_{20}H_{12}N_2O_4$ 367.07 $[M+Na]^+$, observed 367.0.

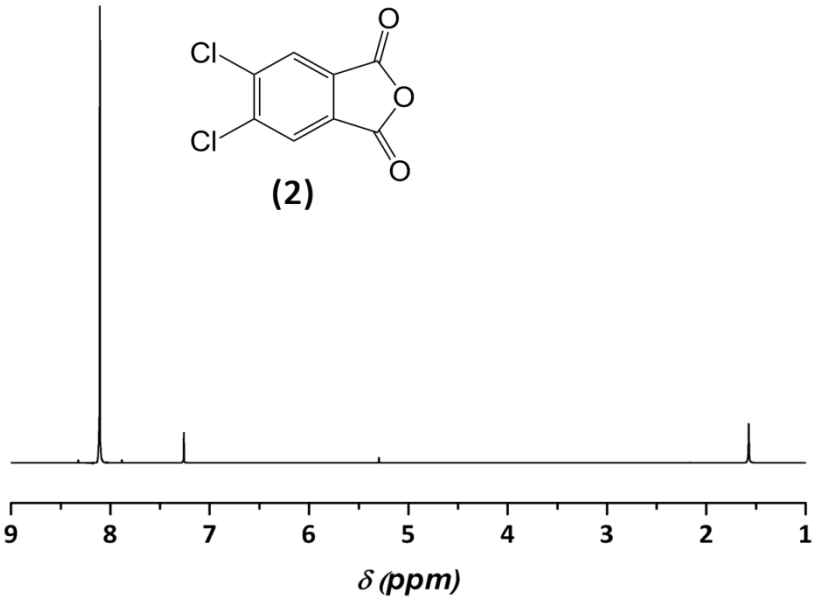

Figure S1 ^{1}H NMR spectrum of 5,6-Dichloro-1,3-isobenzofurandione (**2**)

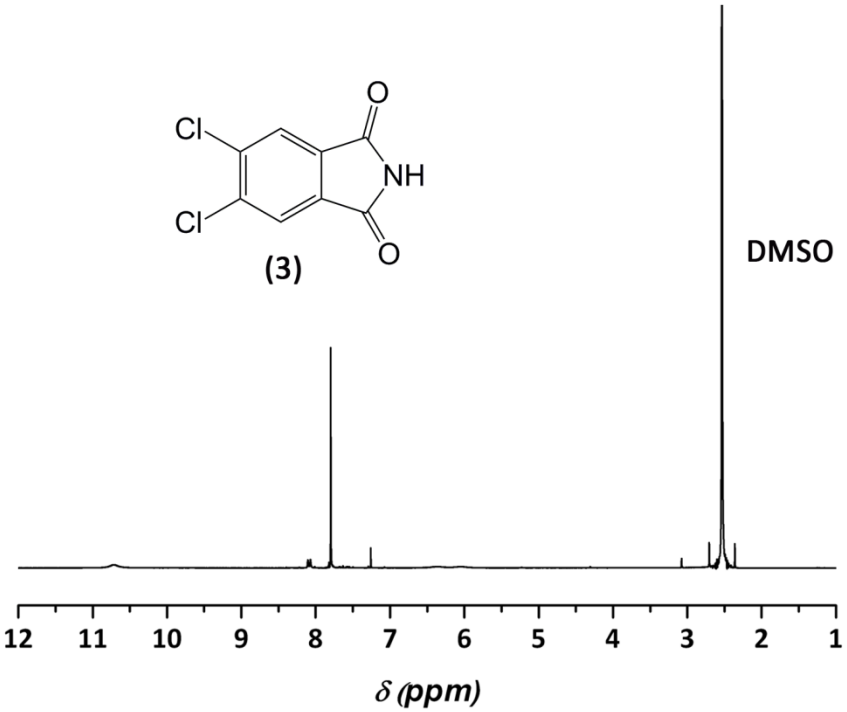

Figure S2 ^{1}H NMR spectrum of 5,6-Dichloro-1*H*-isoindole-1,3(2*H*)-dione (**3**)

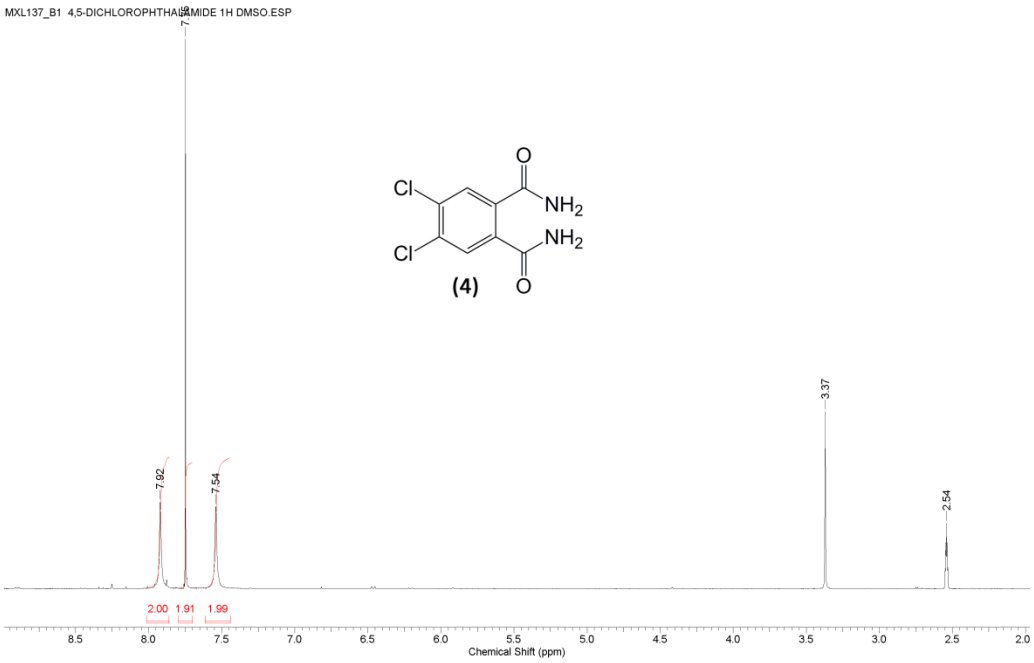

Figure S3 ^{1}H NMR spectrum of 4,5-Dichloro-1,2-benzenedicarboxamide (**4**)

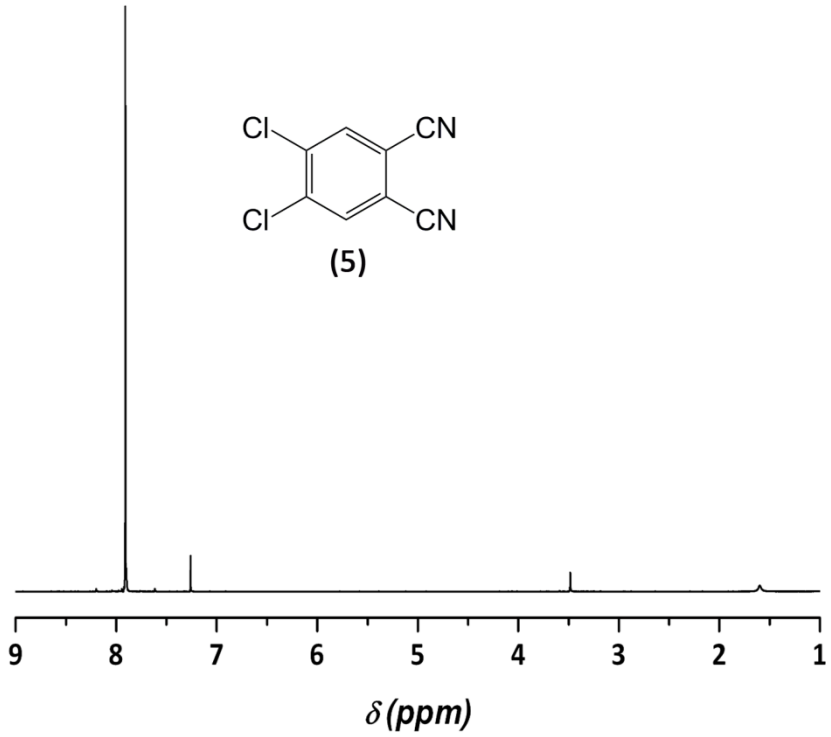

Figure S4 ^{1}H NMR spectrum of 4,5-Dichloro-1,2-dicyanobenzene (**5**)

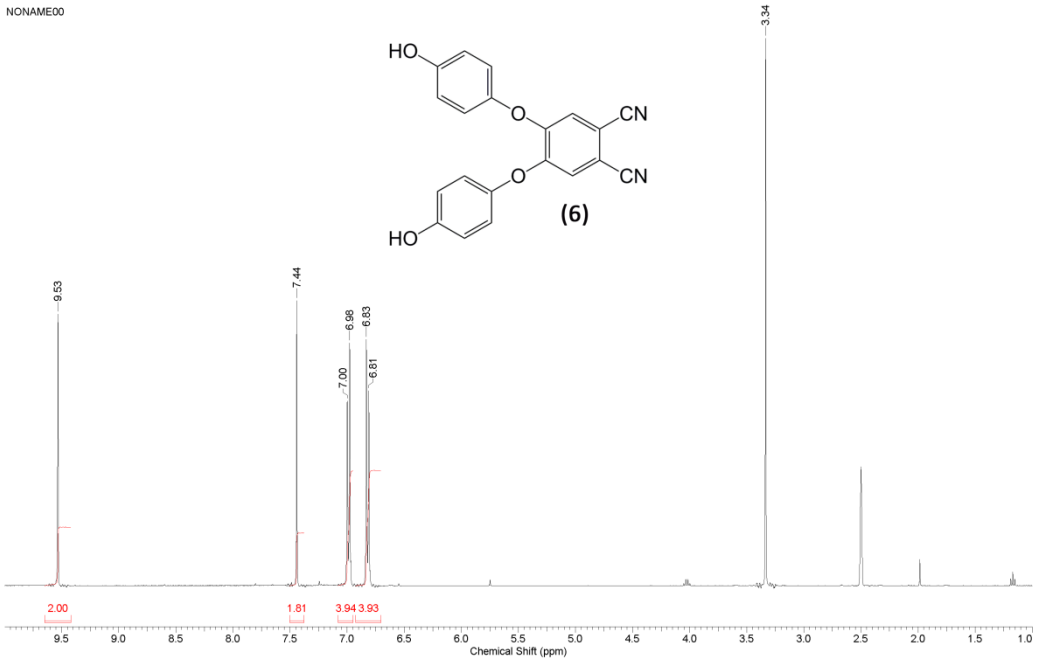

Figure S5 ^{1}H NMR spectrum of 4,5-Bis(4-hydroxyphenoxy)phthalonitrile (**6**)

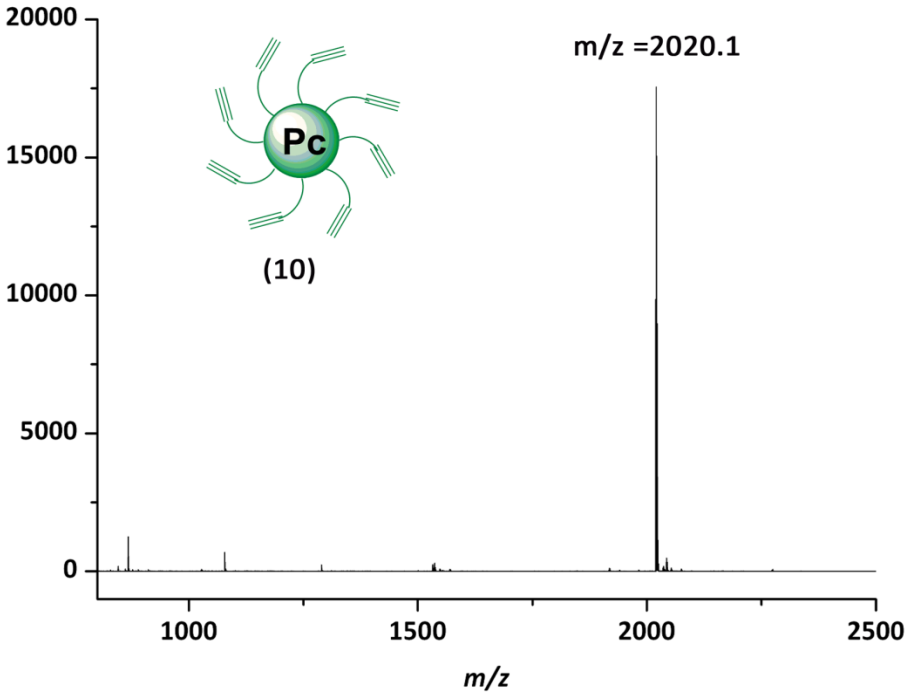

Figure S6 MALDI-ToF characterisation of 2,3,9,10,16,17,23,24-Octa(6-(triisopropylsilyl)hex-5-ynyloxy)phenoxy)phthalocyanine (**10**)