

Supporting information for:

Bis-porphyrin bearing diketopyrrolopyrrole unit – synthesis and physicochemical properties

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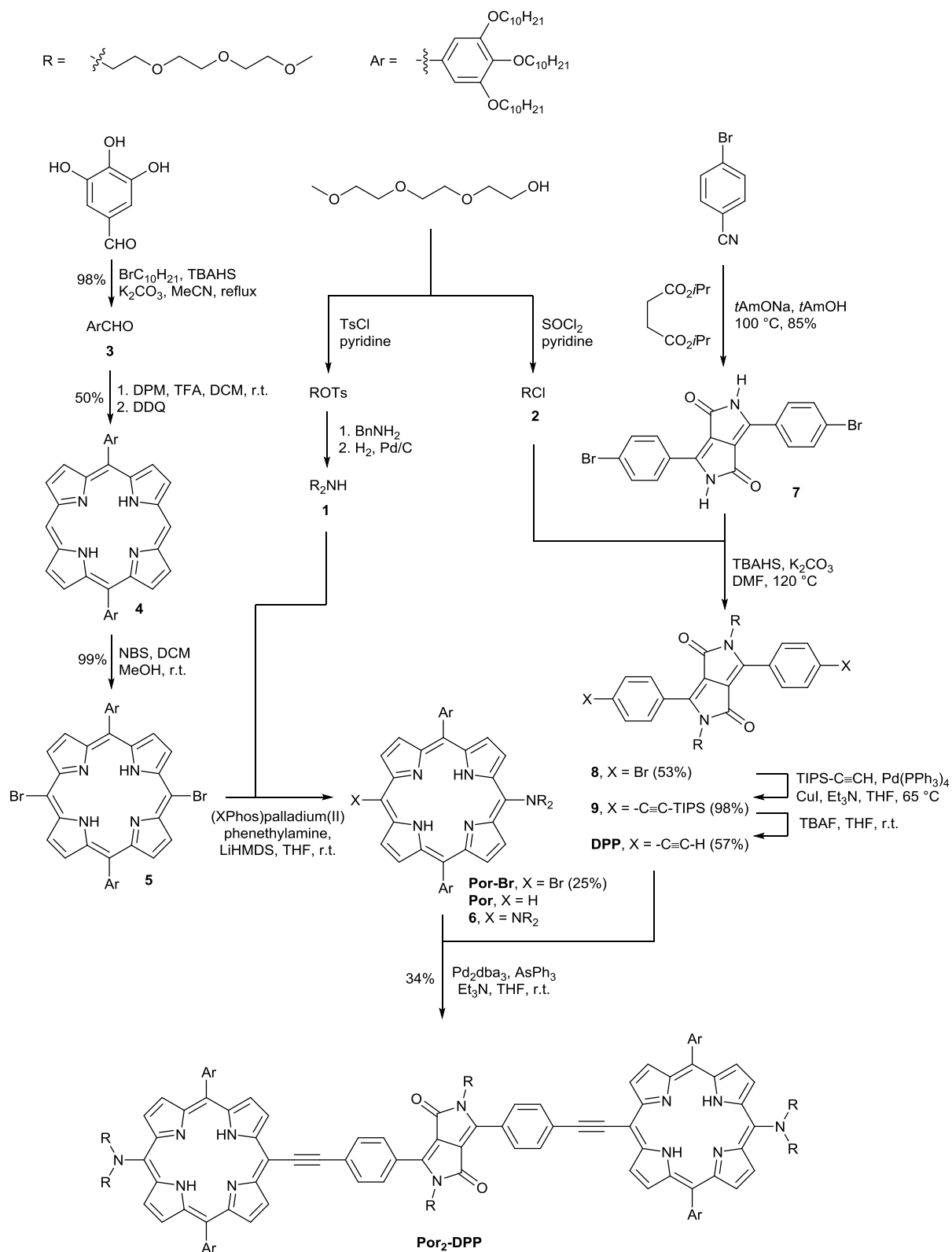
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1. Synthetic strategy

Starting from glycol alcohol, we obtained amine **1**¹ in three steps, and alkylating agent **2**² via standard procedures (Scheme S1). The first one was introduced to the porphyrin *meso* position, whereas the latter attached to the nitrogen atoms of DPP in alkylation reaction. The last step assumed coupling of both chromophores. Conceptually the easiest way to prepare the target molecule was to employ Sonogashira reaction. The required building blocks were prepared as follows. Dipyrromethane was synthesized according to the literature procedure.³ To obtain tris(decyloxy)benzaldehyde **3** PTC methodology⁴ was applied using decyl bromide as alkylating agent and tetrabutylammonium bisulfate (TBAHS) as PTC catalyst. This procedure turned out to be superior to the previously reported⁵ due to the fact that mono-alkylated and bis-alkylated intermediates were rapidly transformed in the final tris-substituted product, which eliminated tedious chromatography aimed at separation of the desired aldehyde **3** from the products of incomplete alkylation. The following [2+2] condensation between dipyrromethane and aldehyde **3** afforded porphyrin **4**, which upon bromination with NBS gave dibromo product **5** in 99% yield.⁶ The following Buchwald-Hartwig amination of this compound provided monoaminoporphyrin **Por-Br**. The reaction was very sensitive to the applied conditions. Several attempts to prepare compound **Por-Br** using slightly changed procedure resulted in a different outcome of the reaction. In some cases significant amount of debrominated product **Por** was observed as a result of Pd-mediated dehalogenation, and porphyrin **Por** was isolated along with the desired porphyrin **Por-Br**.

As those two compound do not differ much in either R_f or size, separation one from another was an extremely arduous and time-consuming task. It required several SEC chromatographies. Use of a higher amount of amine **1** and prolongation of the reaction time allowed to obtain diamino product **6** in 30% yield. DPP pigment **7** containing two exchangeable bromine atoms was prepared by the condensation of *p*-bromobenzonitrile and diisopropyl succinate (DIPS) using sodium *tert*-amylate as a base (Scheme S1).⁷ An attempt of the alkylation of resulting pigment with triethylene glycol monomethyl ether tosylate under classical conditions (DMF, K_2CO_3 , 120 °C)⁸ gave only traces of desired product **8**. However, the yield was significantly increased (to 53%) when tosylate was exchanged with 1-chloro-2-(2-(2-methoxyethoxy)ethoxy)ethane (**2**) and the reaction was performed in the presence of TBAHS as the phase-transfer catalyst. The improvement of alkylation yield of DPP after the addition of TBAHS was observed previously in our research group in case of π -expanded DPP synthesis.⁹ Sonogashira coupling of **8** and triisopropylsilylacetylene resulted in compound **9** which after deprotection with TBAF gave dye **DPP** bearing two ethynyl substituents. It is noteworthy that aminoporphyrins **Por-Br**, **Por**, and **6**, together with the final product **Por₂-DPP** are prone to decomposition under acidic conditions, such as that provided by $CDCl_3$ in an NMR tube. Moreover performing SEC in THF is also not advised for the same reason. Better alternative is to purify amino compounds by SEC in toluene and measure NMR spectra in more neutral solvents.

The synthesis of the final compound **Por₂-DPP** is depicted in Scheme S1.



Scheme S1. Synthesis of the target molecule.

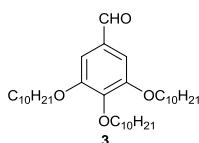
2. Experimental procedures and references

(I) General

All chemicals were used as received unless otherwise noted. All reported ^1H NMR and ^{13}C NMR spectra were recorded on 400, 500 or 600 MHz spectrometer. Chemical shifts (δ ppm) were determined with TMS as the internal reference; J values are given in Hz. UV/vis and fluorescence spectra were recorded in chloroform. Chromatography was performed on silica (Kieselgel 60, 200-400 mesh). SEC was performed on Bio-Beads SX-1 in toluene or THF. Bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)amine (**1**),¹ 1-chloro-2-(2-(2-methoxyethoxy)ethoxy)ethane (**2**),² 5,15-bis[3,4,5-tris(decyloxy)phenyl]porphyrin (**4**),⁶ 5,15-dibromo-10,20-bis[3,4,5-tris(decyloxy)phenyl]porphyrin (**5**),⁶ and 1,4-diketo-3,6-bis(4-bromophenyl)-pyrrolo[3,4-*c*]pyrrole (**7**)⁷ were prepared according to the literature procedures.

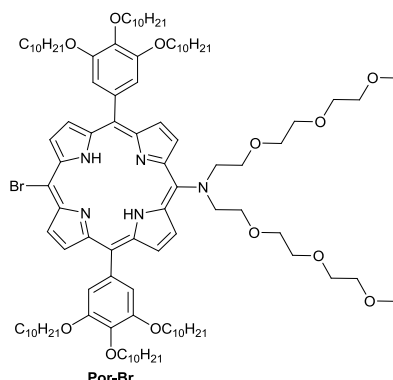
(II) Synthesis

3,4,5-Tris(decyloxy)benzaldehyde (**3**).



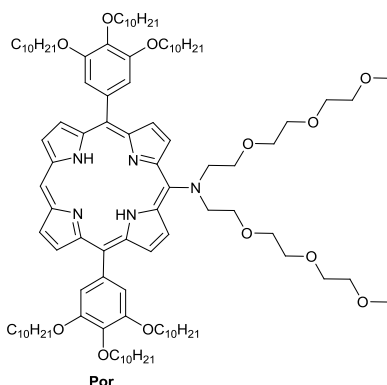
To the solution of 3,4,5-trihydroxybenzaldehyde monohydrate (3.10 g, 18.0 mmol) in MeCN (150 ml), K_2CO_3 (24.9 g, 0.18 mol), and TBAHS (306 mg, 0.9 mmol) were added, followed by 1-bromodecane (16.8 ml, 81 mmol). The reaction mixture was refluxed for 20 h, then it was allowed to cool to r.t.. Subsequently, water was added to the mixture and it was extracted with CHCl_3 and CH_2Cl_2 (3 x 30 ml). The organic layers were combined, washed with brine with AcOH, dried (Na_2SO_4), filtered and evaporated affording brown oil. The crude product was chromatographed (silica, hexanes/EtOAc 9:1) to obtain pure aldehyde **3** (10.18 g, 98%) as a white solid. ^1H NMR (400 MHz, CDCl_3): δ 0.88 (t, $J = 6.8$ Hz, 9H, CH_3), 1.19-1.41 (m, 36H, CH_2), 1.48 (m, 6H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.75 (m, 2H, OCH_2CH_2), 1.83 (m, 4H, OCH_2CH_2), 4.02-4.07 (m, 6H, OCH_2), 7.08 (s, 2H, ArH), 9.83 (s, 1H, CHO). Other spectral and physical properties concur with published data.⁵

5-Bromo-10,20-bis[3,4,5-tris(decyloxy)phenyl]-15-[bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-amino]porphyrin (Por-Br).



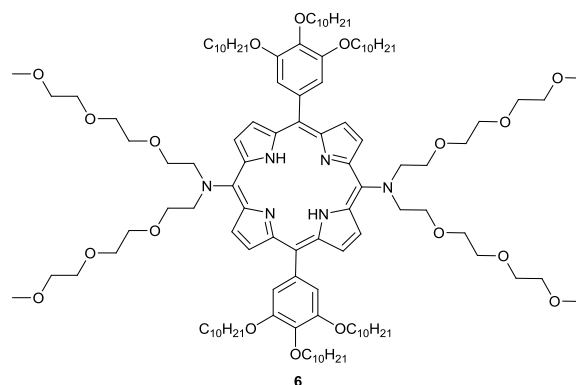
To porphyrin **5** (103 mg, 0.066 mmol), placed in the round-bottomed flask purged with argon, amine **1** (50 mg, 0.162 mmol), and (XPhos)palladium(II) phenethylamine (5 mg, 6.8 μ mol) were added, followed by anhydrous THF (1.1 ml) and LiHMDS (1 M in toluene, 0.32 ml, 0.32 mmol). The reaction mixture was stirred at r.t. for 1 h, then another portion of LiHMDS (1 M in toluene, 0.32 ml, 0.32 mmol) was added and the stirring was continued for 20 h. The reaction mixture was poured into aqueous solution of NH_4Cl . The water layer was extracted with CH_2Cl_2 . The combined organic extracts were dried (Na_2SO_4), filtered and evaporated. The crude product was chromatographed on silica gel (hexanes/EtOAc 4:1) and then by SEC (toluene) to obtain pure porphyrin **Por-Br** (30 mg, 25%) as brown dense oil. Isolation of trace amounts of diaminoporphyrin **6** was discarded. $R_f = 0.55$ (hexane/EtOAc 7:3). UV/vis (CHCl_3) λ (ϵ) = 427 (149 000), 523 (8 600), 582 (6 300), 674 nm (2 600). ^1H NMR (500 MHz, CDCl_3): δ -2.61 (br s, 2H, NH), 0.80-0.96 (m, 18H, CH_3), 1.16-1.53 (m, 80H, CH_2), 1.68 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.88 (m, 8H, OCH_2CH_2), 1.98 (m, 4H, OCH_2CH_2), 3.23 (s, 6H, OCH_3), 3.32-3.38 (m, 4H, OCH_2), 3.45-3.51 (m, 4H, OCH_2), 3.54 (s, 8H, OCH_2), 3.81 (t, $J = 5.9$ Hz, 4H, OCH_2), 4.11 (t, $J = 6.5$ Hz, 8H, OCH_2), 4.30 (t, $J = 6.5$ Hz, 4H, OCH_2), 4.59 (t, $J = 5.9$ Hz, 4H, NCH_2), 7.38 (s, 4H, ArH), 8.83 (d, $J = 4.5$ Hz, 2H, β -H), 8.91 (d, $J = 5.0$ Hz, 2H, β -H), 9.49 (m, 2H, β -H), 9.55 (d, $J = 4.8$ Hz, 2H, β -H). LR MS (FD) calcd for $\text{C}_{106}\text{H}_{170}\text{BrN}_5\text{O}_{12}$ 1784.2, found 1784.3; isotope profiles match.

**5,15-Bis[3,4,5-tris(decyloxy)phenyl]-10-[bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)amino]-
porphyrin (Por).**



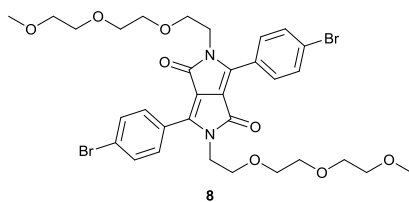
Product **Por**, formed due to palladium-mediated dehalogenation of compound **Por-Br**, was isolated from the mixture of **Por** and **Por-Br** by chromatography on silica gel (silica, hexanes/EtOAc 4:1) and by multiple SEC (toluene). $R_f = 0.54$ (hexane/EtOAc 7:3). UV/vis (CHCl_3) λ (ϵ) = 419 (193 000), 516 (14 200), 659 nm (3 600). Fluorescence (CHCl_3) $\lambda = 687$ nm. ^1H NMR (500 MHz, CDCl_3): δ -2.89 (br s, 2H, NH), 0.85 (t, $J = 6.9$ Hz, 12H, CH_3), 0.93 (t, $J = 6.9$ Hz, 6H, CH_3), 1.21-1.41 (m, 68H, CH_2), 1.48-1.55 (m, 12H, CH_2), 1.69 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.90 (m, 8H, OCH_2CH_2), 2.00 (m, 4H, OCH_2CH_2), 3.24 (s, 6H, OCH_3), 3.34-3.38 (m, 4H, OCH_2), 3.48-3.51 (m, 4H, OCH_2), 3.55 (m, 8H, OCH_2), 3.84 (t, $J = 6.0$ Hz, 4H, OCH_2), 4.13 (t, $J = 6.5$ Hz, 8H, OCH_2), 4.32 (t, $J = 6.6$ Hz, 4H, OCH_2), 4.63 (t, $J = 5.9$ Hz, 4H, NCH_2), 7.44 (s, 4H, ArH), 8.95 (d, $J = 4.8$ Hz, 2H, β -H), 9.04 (d, $J = 4.6$ Hz, 2H, β -H), 9.23 (d, $J = 4.6$ Hz, 2H, β -H), 9.61 (d, $J = 4.7$ Hz, 2H, β -H), 10.05 (s, 1H, *meso*-H). ^{13}C NMR (125 MHz, CDCl_3): δ 14.08, 14.11, 14.2, 22.66, 22.69, 22.8, 25.9, 26.2, 26.4, 28.7, 29.0, 29.2, 29.3, 29.5, 29.6, 29.65, 29.69, 29.78, 29.79, 29.9, 30.2, 30.3, 30.6, 31.0, 31.4, 31.89, 31.92, 32.0, 34.3, 36.5, 58.9, 61.5, 64.6, 69.4, 70.3, 70.5, 70.6, 70.8, 71.8, 73.8, 104.0, 114.4, 119.3, 124.0, 124.8, 129.5, 130.9, 135.9, 136.7, 138.0, 151.1, 151.3, 151.4. HR MS (ESI) calcd for $\text{C}_{106}\text{H}_{172}\text{N}_5\text{O}_{12}$ $[\text{M}+\text{H}]^+$ 1707.3003, found 1707.3043; isotope profiles match.

5,15-Bis[3,4,5-tris(decyloxy)phenyl]-10,20-bis[bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)amino]-porphyrin (6).



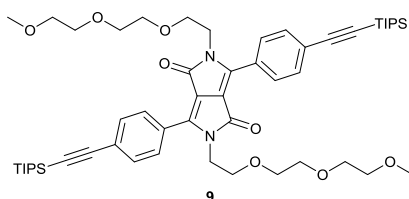
A dry Schlenk tube, which was equipped with a magnetic stir bar and purged with argon, was charged with porphyrin **5** (175 mg, 0.112 mmol). The vessel was evacuated and backfilled with argon (this process was repeated 3 times). Then, anhydrous THF (2.1 ml), amine **1** (95 mg, 0.307 mmol), and (XPhos)palladium(II) phenethylamine (10 mg, 0.014 μ mol) were added, followed by LiHMDS (1 M in toluene, 0.54 ml, 0.54 mmol). The reaction mixture was stirred at r.t. for 19 h. Subsequently, another portion of LiHMDS (1 M in toluene, 0.50 ml, 0.50 mmol) was added and stirring was continued for 24 h. Then, the reaction mixture was diluted with CH_2Cl_2 and washed with aqueous solution of NH_4Cl . The water layer was extracted with CH_2Cl_2 . Organic extracts were combined, dried (Na_2SO_4), filtered and evaporated. The crude product was chromatographed on silica gel (hexanes/EtOAc 4:1 then 1:1). Porphyrin **6** was purified by SEC (THF) to obtain brown oily compound (68 mg, 30%). $R_f = 0.53$ (hexane/EtOAc 11:9). UV/vis (CHCl_3) λ (ϵ) = 427 (174 000), 523 (10 000), 587 (9 000), 675 nm (4 100). Fluorescence (CHCl_3) $\lambda = 725$ nm. ^1H NMR (500 MHz, CDCl_3): δ -2.62 (br s, 2H, NH), 0.86 (t, $J = 6.9$ Hz, 12H, CH_3), 0.93 (t, $J = 7.1$ Hz, 6H, CH_3), 1.22-1.47 (m, 68H, CH_2), 1.52 (m, 12H, CH_2), 1.69 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.89 (m, 8H, OCH_2CH_2), 1.99 (m, 4H, OCH_2CH_2), 3.25 (s, 12H, OCH_3), 3.37-3.41 (m, 8H, OCH_2), 3.49-3.59 (m, 24H, OCH_2), 3.81 (t, $J = 6.0$ Hz, 8H, OCH_2), 4.12 (t, $J = 6.4$ Hz, 8H, OCH_2), 4.31 (t, $J = 6.5$ Hz, 4H, OCH_2), 4.55 (t, $J = 5.9$ Hz, 8H, NCH_2), 7.41 (s, 4H, ArH), 8.83 (d, $J = 4.5$ Hz, 4H, β -H), 9.47 (d, $J = 4.0$ Hz, 4H, β -H). ^{13}C NMR (125 MHz, CDCl_3): δ 11.0, 14.0, 14.1, 14.2, 22.7, 22.8, 23.0, 23.8, 26.2, 26.4, 28.9, 29.3, 29.49, 29.51, 29.6, 29.7, 29.8, 29.9, 30.4, 30.6, 31.9, 32.0, 38.7, 58.9, 61.2, 68.2, 69.4, 70.3, 70.5, 70.6, 70.8, 71.8, 73.8, 114.3, 119.4, 128.4, 128.8, 130.9, 132.5, 137.2, 137.9, 151.2, 167.7. HR MS (ESI) calcd for $\text{C}_{120}\text{H}_{202}\text{N}_6\text{O}_{18}$ $[\text{M}+2\text{H}]^{2+}$ 1007.7532, found 1007.7524; isotope profiles match. Elemental analysis calcd (%) for $\text{C}_{120}\text{H}_{200}\text{N}_6\text{O}_{18}$: C, 71.53; H, 10.00; N, 4.17; found: C, 71.58; H, 10.21; N, 4.03.

2,5-Bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-1,4-diketo-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole (8).



A mixture of 1,4-diketo-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole (**7**) (2.01 g, 4.5 mmol), TBAHS (76 mg, 0.22 mmol), powdered potassium carbonate (9.40 g, 68 mmol) and 100 ml of DMF was heated to 120 °C under an argon atmosphere. Then 1-chloro-2-(2-(2-methoxyethoxy)ethoxy)ethane (8.22 g, 45 mmol) was added dropwise by a syringe (30 min). The reaction mixture was stirred for 16 h at 120 °C, cooled and diluted with 150 ml of water. The obtained suspension was passed through Celite, which was washed with several portions of water in order to remove DMF and inorganic salts. Celite was then washed with chloroform until the fluorescence of filtrates disappeared. To the combined organic filtrates water was added and layers were separated. The aqueous layer was extracted with 4 portions of chloroform. Combined organic layers were washed twice with water and dried over sodium sulfate. Solvents were evaporated and the crude product was obtained as a red solid. Recrystallization from ethanol gave pure **8** (1.77 g, 53%) as red fibrous crystals. Mp: 150-152 °C. ¹H NMR (500 MHz, CDCl₃): δ 3.36 (s, 6H, OCH₃), 3.47-3.53 (m, 4H, OCH₂), 3.54-3.60 (m, 12H, OCH₂), 3.75 (t, *J* = 5.3 Hz, 4H, OCH₂), 3.90 (t, *J* = 5.3 Hz, 4H, NCH₂), 7.63-7.69 (m, 4H, ArH), 7.90-7.96 (m, 4H, ArH). ¹³C NMR (125 MHz, CDCl₃): δ 42.4, 59.1, 68.9, 70.5, 70.6 (2 signals), 71.9, 109.7, 125.9, 126.8, 131.0, 132.1, 148.2, 162.8. HR MS (ESI) calcd for C₃₂H₃₈Br₂N₂O₈Na [M+Na]⁺ 759.0887, found 759.0866. Elemental analysis calcd (%) for C₃₂H₃₈Br₂N₂O₈: C 52.05, H 5.19, N 3.79; found: C 51.98, H 5.15, N 3.61.

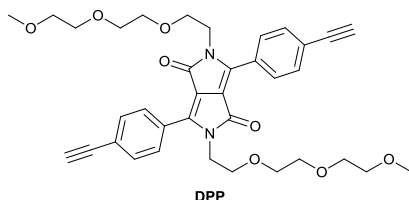
2,5-Bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-1,4-diketo-3,6-bis(4-((triisopropylsilyl)ethynyl)phenyl)pyrrolo[3,4-c]pyrrole (9).



In a 20 ml Schlenk flask containing a magnetic stirring bar were placed: 2,5-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-1,4-diketo-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole (**8**, 369 mg, 0.50 mmol), tetrakis(triphenylphosphine)palladium(0) (29 mg, 25 μmol), and copper(I) iodide (9.5

mg, 50 μmol). The vessel was evacuated and backfilled with argon (3 times). Then triisopropylsilylacetylene (340 μl , 1.5 mmol), triethylamine (280 μl , 2.0 mmol), and anhydrous THF (10 ml) were added under a positive pressure of argon. The flask was again carefully evacuated and backfilled with argon three times. The vessel was tightly closed and the reaction mixture was stirred for 16 h at 65 $^{\circ}\text{C}$. After the mixture was cooled, water and dichloromethane were added, layers were separated. The aqueous layer was extracted with dichloromethane 3 times. Combined organic layers were washed with water and dried over Na_2SO_4 . Solvents were evaporated and the product was purified using the column chromatography (silica, CH_2Cl_2 :acetone 19:1). 462 mg (98%) of **9** was obtained as a red, fluorescent, amorphous solid. Mp: 76-79 $^{\circ}\text{C}$. ^1H NMR (500 MHz, CDCl_3): δ 1.02-1.21 (m, 42H, *i*Pr), 3.35 (s, 6H, OCH_3), 3.47-3.52 (m, 4H, OCH_2), 3.54-3.59 (m, 12H, OCH_2), 3.74 (t, $J = 5.4$ Hz, 4H, OCH_2), 3.93 (t, $J = 5.4$ Hz, 4H, NCH_2), 7.56-7.64 (m, 4H, ArH), 7.93-8.01 (m, 4H, ArH). ^{13}C NMR (125 MHz, CDCl_3): δ 11.3, 18.7, 42.3, 59.0, 68.9, 70.5, 70.6, 71.9, 94.1, 106.6, 110.0, 126.4, 127.5, 129.2, 131.0, 132.3, 148.4, 162.8. HR MS (ESI) calcd for $\text{C}_{54}\text{H}_{80}\text{N}_2\text{O}_8\text{Si}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 963.5351, found 963.5347.

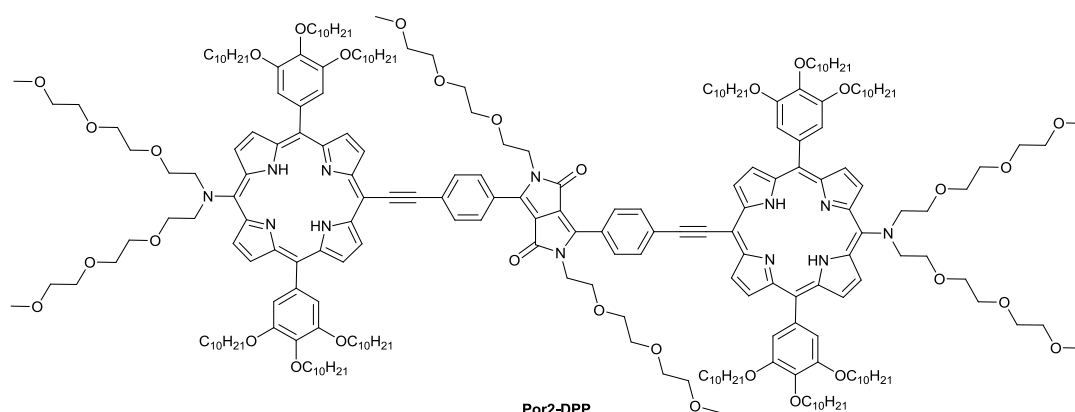
2,5-Bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-1,4-diketo-3,6-bis(4-ethynylphenyl)pyrrolo-[3,4-c]pyrrole (DPP).



Under an argon atmosphere 2,5-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-1,4-diketo-3,6-bis(4-((triisopropylsilyl)ethynyl)phenyl)pyrrolo[3,4-c]pyrrole (**9**, 424 mg, 0.45 mmol) was dissolved in 15 ml of anhydrous THF. Then 1 M solution of tetrabutylammonium fluoride in THF (TBAF, 2.0 ml, 2.0 mmol) was added and the reaction mixture was stirred for 1 h at room temperature. Water and dichloromethane were added and layers were separated. The aqueous layer was extracted with 3 portions of dichloromethane. Combined organic layers were washed twice with water and dried over sodium sulfate. Solvents were evaporated, and the product was isolated by the column chromatography (CH_2Cl_2 :acetone 19:1) and recrystallized from CHCl_3 /MeOH to give 162 mg (57%) of **DPP** as a bright orange powder. Mp: 144-146 $^{\circ}\text{C}$. UV/vis (CHCl_3) λ (ϵ) = 484 nm (20 000). Fluorescence (CHCl_3) λ = 549 nm. ^1H NMR (500 MHz, CDCl_3): δ 3.22 (s, 2H, $\text{C}\equiv\text{CH}$), 3.35 (s, 6H, OCH_3), 3.48-3.52 (m, 4H, OCH_2), 3.54-3.59 (m, 12H, OCH_2), 3.75 (t, $J = 5.4$ Hz, 4H, OCH_2), 3.93 (t, $J = 5.4$ Hz, 4H, NCH_2), 7.60-7.66 (m, 4H, ArH), 7.98-8.03 (m, 4H, ArH). ^{13}C NMR

(125 MHz, CDCl₃): δ 42.4, 70.5, 59.0, 68.9, 70.6, 71.9, 79.7, 83.1, 110.0, 125.0, 128.1, 129.3, 132.4, 148.4, 162.8. HR MS (ESI) calcd for C₃₆H₄₀N₂O₈Na [M+Na]⁺ 651.2682, found 651.2687.

Bis-porphyrin Por₂-DPP.



A Schlenk tube was charged with porphyrin **Por-Br** (20 mg, 0.011 mmol), dried and purged with argon. Then, **DPP** (3 mg, 4.8 μ mol) was added, followed by anhydrous THF (1.6 ml), and Et₃N (0.8 ml, 5.7 mmol). Next, the vessel was carefully evacuated and backfilled with argon (this process was repeated 3 times). To the degassed mixture AsPh₃ (24 mg, 0.078 mmol) and Pd₂dba₃ (14 mg, 0.014 mmol) were added. The reaction mixture was stirred at r.t. for 5 d, filtered through a short pad of Celite, and evaporated. The crude product was chromatographed (silica, hexane/EtOAc 4:1 to 13:7) to give **Por₂-DPP**, contaminated by another green compound of higher polarity. This impurity was removed by SEC (toluene) yielding pure bis-porphyrin **Por₂-DPP** (6.5 mg, 34%) as green glass. R_f = 0.36 (silica, heksan/EtOAc 1:1). UV/vis (CHCl₃) λ (ϵ) = 440 (303 000), 605 (67 700), 520 (61 300), 681 nm (32 700). Fluorescence (CHCl₃) λ = 705 nm. ¹H NMR (500 MHz, CDCl₃): δ -2.03 (br s, 4H, NH), 0.85 (t, J = 7.1 Hz, 24H, CH₃), 0.93 (t, J = 7.0 Hz, 12H, CH₃), 1.15-1.47 (m, 120H, CH₂), 1.47-1.61 (m, 40H, CH₂), 1.65-1.73 (m, 8H, OCH₂CH₂CH₂), 1.90 (m, 16H, OCH₂CH₂), 2.00 (m, 8H, OCH₂CH₂), 3.24 (s, 12H, OCH₃), 3.37 (m, 8H, OCH₂), 3.38 (s, 6H, OCH₃), 3.50 (m, 8H, OCH₂), 3.55 (m, 16H, OCH₂), 3.57-3.61 (m, 4H, OCH₂), 3.66-3.73 (m, 12H, OCH₂), 3.84 (t, J = 6.0 Hz, 8H, OCH₂), 3.92 (t, J = 5.5 Hz, 4H, OCH₂), 4.14 (m, 20H, OCH₂ + NCH₂), 4.32 (t, J = 6.5 Hz, 8H, OCH₂), 4.63 (t, J = 5.6 Hz, 8H, NCH₂), 7.42 (s, 8H, ArH), 8.17 (AA'BB', J = 8.5 Hz, 4H, ArH), 8.32 (AA'BB', J = 8.4 Hz, 4H, ArH), 8.78 (d, J = 4.5 Hz, 4H, β -H), 8.95 (m, 4H, β -H), 9.45 (d, J = 3.8 Hz, 4H, β -H), 9.63 (d, J = 4.6 Hz, 4H, β -H). ¹³C NMR (125 MHz, CDCl₃): δ 14.1, 22.7, 22.8, 26.2, 26.3, 29.3, 29.49, 29.57, 29.65, 29.69, 29.78, 29.88, 30.3, 30.6, 31.9, 32.0, 58.90, 58.91, 59.1, 61.1, 69.1, 69.4, 70.3, 70.5, 70.64, 70.69, 70.73, 71.8, 72.0, 73.8, 95.4, 96.2, 97.6, 110.3, 113.7, 114.3, 121.2, 124.8, 127.1, 127.6, 129.8, 131.75, 131.81, 136.6, 138.1, 148.5, 151.4, 163.1.

HR MS (ESI) calcd for $C_{248}H_{382}N_{12}O_{32}$ $[M+4H]^{4+}$ 1010.2158, found 1010.2154; isotope profiles match.

(III) Literature

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3. Structural analysis: POM, XRD, and IR data

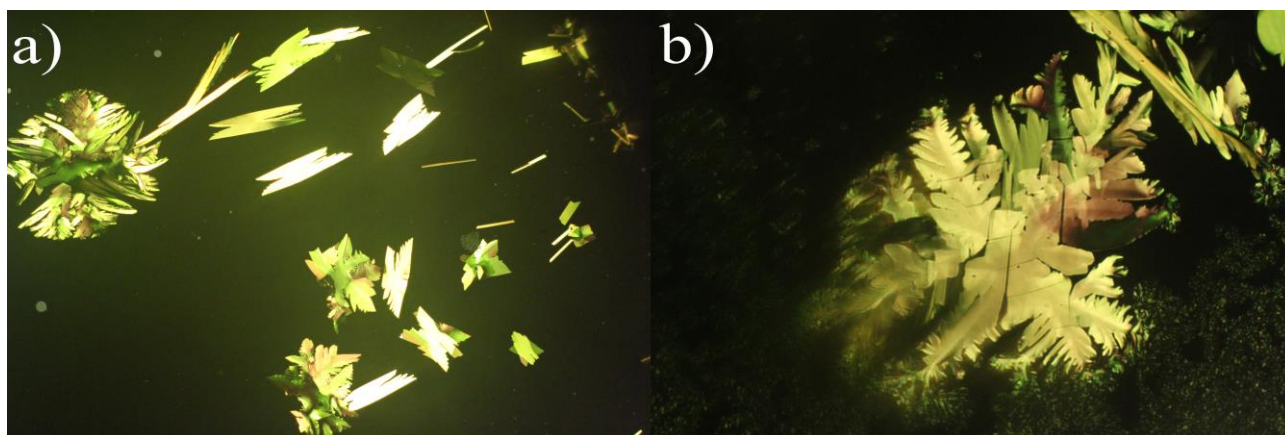


Fig. S1 Crystal shapes observed on cooling a) at temperature just below phase transition, and b) at 130 °C.

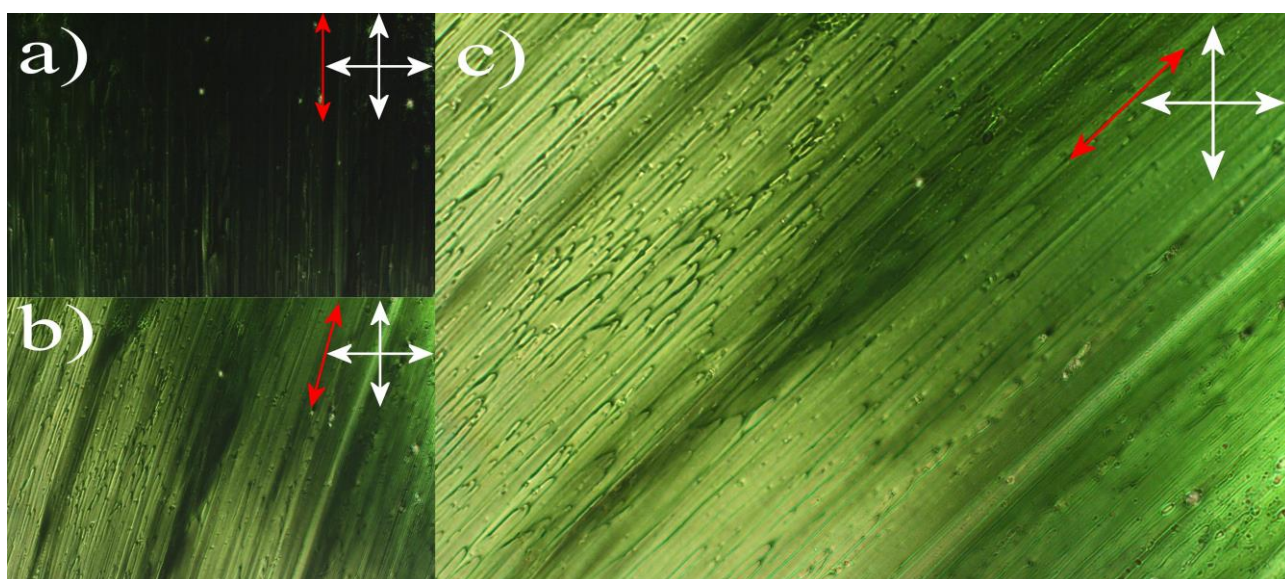


Fig. S2 POM image of weakly sheared crystal. Shearing direction a) parallel/perpendicular, b) inclined, and c) at 45° to polarizers axes (white arrows).

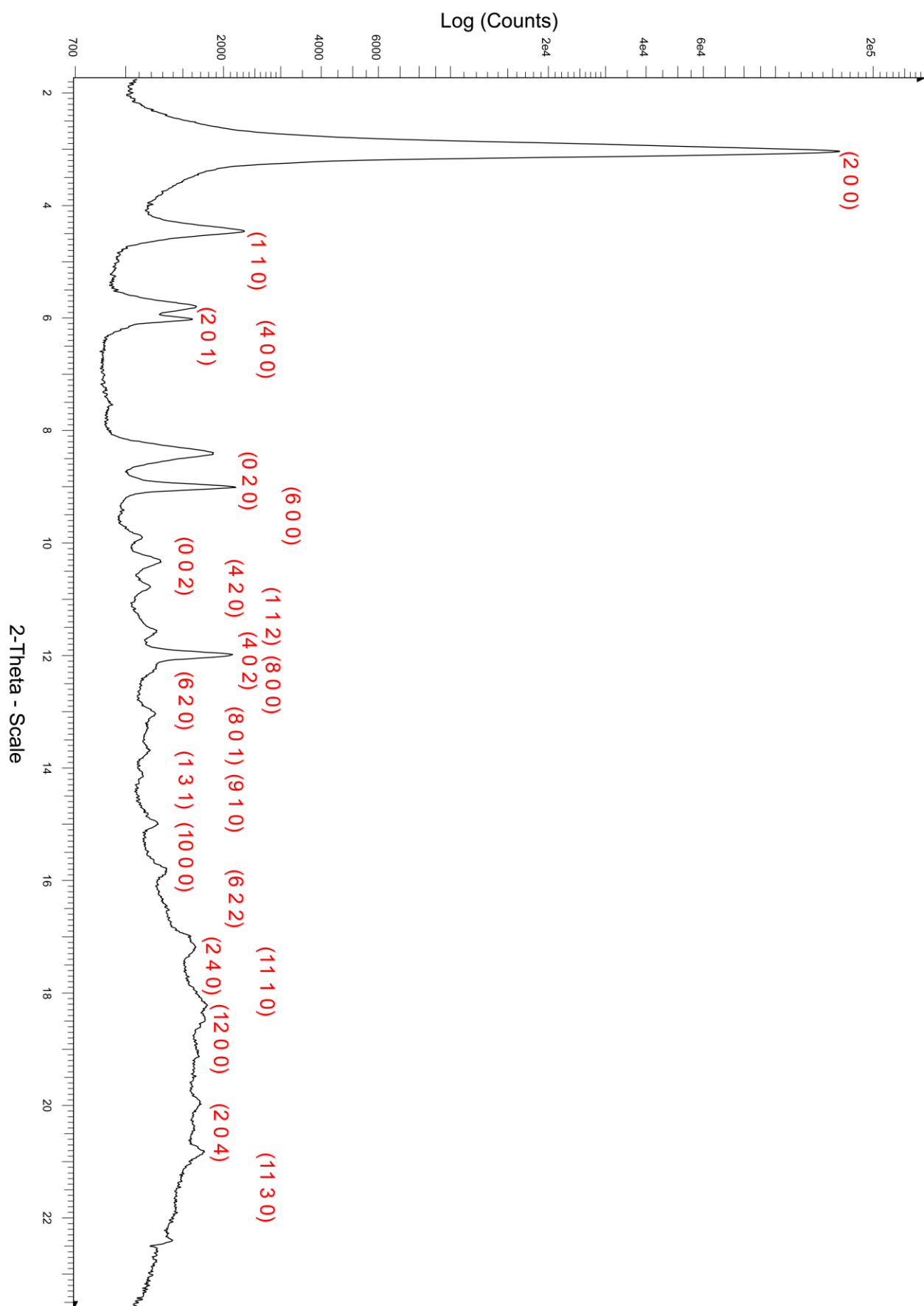


Fig. S3 X-ray diffraction pattern of **Por₂-DPP**, indexing assumes C2221 space group with crystallographic unit cell parameters: a = 58.8 Å, b = 21.1 Å, c = 18.0 Å.

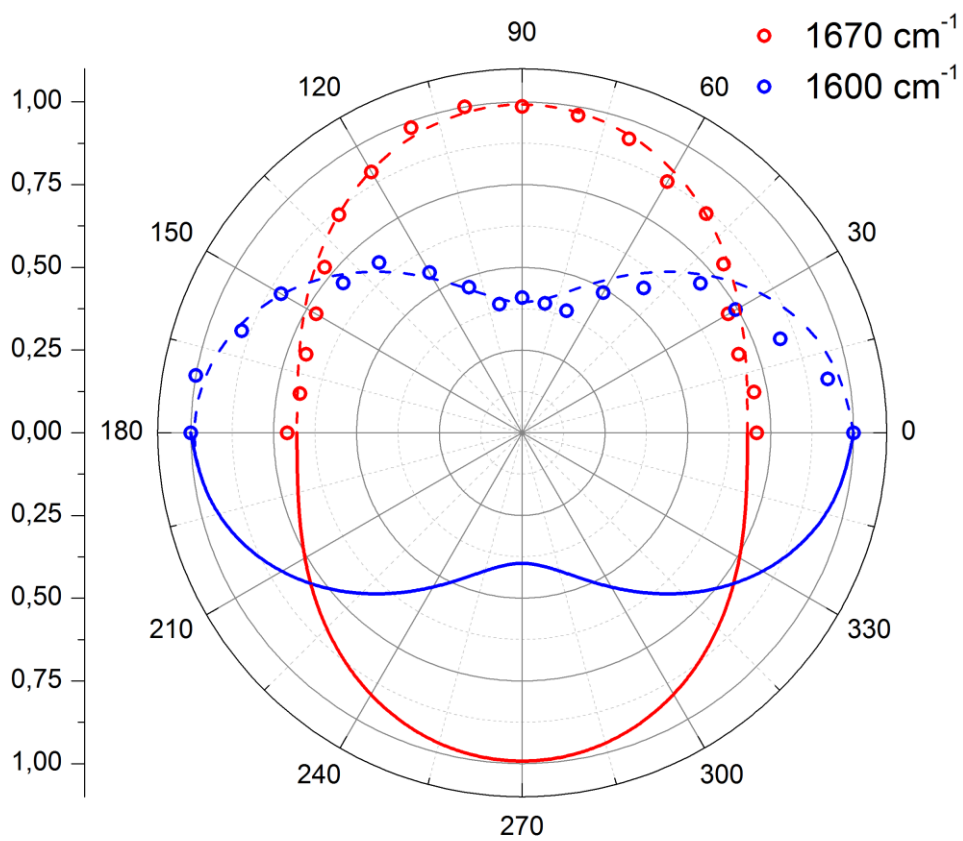


Fig. S4 Normalized IR absorbance vs. polarization direction of incident beam for C=O (1670cm⁻¹) and C=C (in DPP unit 1600cm⁻¹) stretching vibrations. Shearing direction is along 90 deg direction.

4. Spectral data

