

Design and efficient synthesis of a new scaffold based on unsymmetrical protoporphyrin IX derivatives for use in SPPS.

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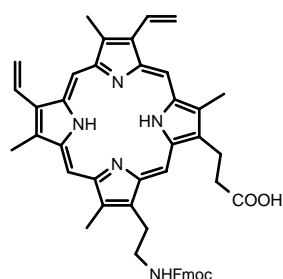
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Electronique Supplementary Informations

Chemistry

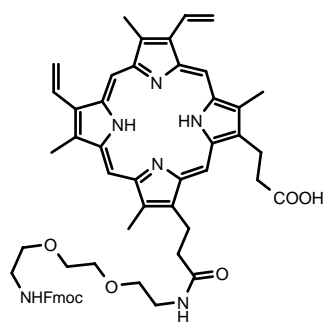
Compound 5 :



5

Resin **4** (83 mg; 36.5 μmol .) was treated with 20 mL of TFA/DCM/TIS (50: 49: 1) mixture at rt for 4 h. Resin was then filtered and washed with TFA (2 x 10 mL). Filtrate and washings were concentrated (to #2 mL) under reduced pressure, then Et₂O (30mL) was added. The precipitate was filtered off, washed with CHCl₃ (4 x 20 mL) and dried under high vacuum, providing **5** (isomeric mixture) as a deep purple solid (8 mg; 27%). R_f = 0.33 (DMF/TFA/water; 8:1:1). MALDI-TOF MS calc for C₄₈ H₄₅ N₅ O₄ (MH⁺), 756.89 found, 756.81. Anal. (C₄₈ H₄₅ N₅ O₄), 2H₂O calc C 72.80 , H 6.23 , N 8.84, found C 72.23, H, 6.12 N 8.73 .UV-vis spectrum in DMF: λ_{max} , nm ($\epsilon \times 10^{-3} \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$): 409.6 (90.8), 506.8 (9.6), 542.9 (7.5), 576.0 (5.7), 630.6 (2.9). ¹H NMR (400.13 MHz, d₆ DMSO, 25°C) δ (ppm): -3.8 (broad s, 2H, NH pyrrole); 3.2 (m, 4H, ProtoIX-CH₂ alkyl), 3.5-3.6 (brs, 12H, CH₃ β -pyrrole), 4.3 (m, 4H, -CH₂CO and CH₂NH-), 6.19 (dd, $J = 11.5$ -1.5 Hz ; 2H, =CH₂), 6.37 (dd, $J = 17.8$ -1.5 Hz ; 2H, =CH₂) ; 7.66 (d, $J = 7.5$ Hz ; 6H, H-1,8 ; 2,7; 3,6 Fmoc), 7.86 (d, $J = 7.5$ Hz ; 2H, H-4,5 Fmoc), 8.05 (dd, $J = 11.5$ -17.8 Hz ; 2H, CH=), 10.16 (s, 1H, H-*meso*), 10.21 (s, 1H, H-*meso*), 10.27 (s, 1H, H-*meso*); 10.29 (s, 1H, H-*meso*).

Compound 8 :



8

Resin **7** (79 mg; 56 μmol .) was stirred for 4 h at rt in a mixture of TFA/DCM/TIS (50:49:1), then filtered off and washed with TFA (2 x 10mL). Pooled filtrate and washings were concentrated (to #2 mL) under reduced pressure, then Et₂O (30 mL) was added. The purple solid was filtered off, washed with CHCl₃ (4 x 20 mL) and dried overnight in vacuum, providing 5 mg of **8** (isomeric mixture) as a purple solid (10%). R_f = 0.30 (DMF/TFA/water 8:1:1). MALDI-TOF MS calc for C₅₅ H₅₈ N₆ O₇ (MH⁺), 916.06 found, 916.09. Anal. (C₅₅ H₅₈ N₆ O₇), 2H₂O calc C 69.30 , H 6.55 , N 8.81, found C 69.10, H, 6.38 N 8.71 .UV-vis spectrum in DMF: λ_{max} , nm ($\epsilon \times 10^{-3}$ L.mol⁻¹.cm⁻¹): 390.5 (111.8); 490.9 (5.5) ; 523.3 (4.9) ; 569.8 (4.3) ; 621.0 (2.0)

¹H NMR (400,13 MHz, d₆ DMSO, 25°C) δ (ppm): -3.8 (broad s., 2 H, NH pyrrole) ; 3.5-4.3 (m, 8 H, H_{alkyl}), 3.5-3.6 (brs, 12 H, CH₃ β -pyrrole), 3.39 (m, 2 H, H_a), 3.49 (m, 2 H, H_h), 3.68-3.85 (m, 8 H, H_{b, c, d, e}) ; 4.1 (s, 1 H, NHCO), , 6.19 (dd, $J=11.5-1.5$ Hz, 2 H, =CH₂), 6.36 (dd, $J=17.8-1.5$ Hz, 2 H, =CH₂), 7.66 (d, $J=7.5$ Hz, 6 H, H_{aryliques 1,8 ; 2,7 et 3,6}) ; 7.86 (d, $J=7,5$ Hz, 2 H, H_{aryliques 4,5}), 8.05 (dd, $J=11.5-17.8$ Hz, 2 H, CH=), 10.16 (s, 1 H, H_{meso-}), 10.21 (s, 1 H, H-*meso*), 10.27 (s, 1 H, H-*meso*), 10.29 (s, 1H, H-*meso*).