SUPPORTING INFORMATION


Francisco J. Céspedes-Guirao,† Ana Belén Ropero,‡ Enrique Font-Sanchis,† Ángel Nadal,*,‡ Fernando Fernández-Lázaro,*,† and Ángela Sastre-Santos*,†

División de Química Orgánica and Unidad de Fisiología Celular y Nutrición, Instituto de Bioingeniería, Universidad Miguel Hernández, Elche 03202, Spain

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Materials and methods for the synthesis of 1 and 2.

All reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. Compound 3 was synthesized according to already published procedures. Commercial TLC plates (silica gel 60 F254, SDS) were used to monitor the progress of the reaction, with spots observed under UV light at 254 and 365 nm. Column chromatography was performed with silica gel 60A (particle size 40-63 µm, SDS).

NMR spectra were taken using either a 500 MHz Bruker Avance DRX 500 or a Bruker AC-300. Ultraviolet–visible (UV-vis) absorption measurements were taken on a ThermoSpectronic Helios γ spectrophotometer. Fluorescence measurements were recorded with a Perkin Elmer LS Luminiscence spectrometer. Infrared measurements were taken with a Fourier Transform (FT-IR) ThermoNicolet model IR 200 Spectrometer in transmission mode using KBr pellets. Mass spectra were obtained either from a Bruker Reflex III matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) spectrometer using dithranol and trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix, or with electrospray ionization (ESI) from an API QStar Pulsar-Applied Biosystems. Elemental analyses were performed on a LECO CHNS-932 elemental analyzator.
Synthesis of PBI-1

Synthesis of PBI-3a

PBI-3 (400 mg, 0.47 mmol), 3-hydroxypyridine (357 mg, 3.76 mmol) and anhydrous K$_2$CO$_3$ were added to anhydrous NMP (60 mL). The mixture was stirred at 100 °C under argon for 24 h. After cooling, the reaction mixture was poured into 1M aqueous hydrochloride acid (250 mL) obtaining a red-purple solution (tetrapyridinium salt of PDI). The solution was cooled into an ice bath and aqueous NaHCO$_3$ (saturated) was added until pH 8. NaCl was added to saturation and the mixture was stirred overnight. The precipitated product was filtered under suction and then was dissolved in CH$_2$Cl$_2$/Acetone 9:1. This solution was washed twice with brine and was dried with anhydrous magnesium sulfate. The product was purified by flash chromatography (SiO$_2$, CH$_2$Cl$_2$/MeOH 9:1), yielding 156 mg (30 %) of a red solid.$^1$

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 8.35$ (broad, 8H, H-pyridine), 8.25 (s, 2H, 2xH-PDI), 8.22 (s, 2H, 2xH-PDI), 7.45 (t, 1H, J=7.5 Hz, H-Ar), 7.33 (d, 2H, J=8.2 Hz, 2xH-Ar$^-$), 7.34-7.26 (m, 10H, 8xH-pyridine and 2xH-Ar-H), 7.15 (d, 2H, J=8.2 Hz, 2xH-Ar$^-$), 2.75 (t, 2H, J=7.2 Hz, Ar-CH$_2$-) 2.68 (sept, 2H, J=6.9 Hz, 2xCH-(CH$_3$)$_2$), 2.39 (t, 2H, J=6.9 Hz, CH$_2$-CO$_2$H), 2.01 (m, 2H Ar-CH$_2$-CH$_2$-CH$_2$-CO$_2$H) 1.12 ppm (d, 12H, J=6.9 Hz, 4xCH-(CH$_3$)$_2$). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 176.24, 162.83, 162.63, 155.13, 155.04, 145.80, 145.74, 145.52, 142.34, 141.52, 141.47, 141.46, 141.43, 133.11, 133.08, 132.45, 130.10, 130.09, 129.72, 129.71, 129.53, 129.51, 128.22, 126.84, 126.82, 124.03, 123.71, 123.66, 121.20, 120.95, 120.84, 120.57, 120.56, 113.11, 113.08, 132.45, 130.10, 130.09, 129.72, 129.71, 129.53, 129.51, 128.22, 126.84, 126.82, 124.03, 123.71, 123.66, 121.20, 120.95, 120.84, 120.57, 120.56, 113.11, 113.08, 129.72, 129.71, 129.53, 129.51, 128.22, 126.84, 126.82, 124.03, 123.71, 123.66, 121.20, 120.95, 120.84, 120.57, 120.56, 113.11, 113.08, 129.72, 129.71, 129.53, 129.51, 128.22, 126.84, 126.82, 124.03, 123.71, 123.66, 121.20, 120.95, 120.84, 120.57, 120.56, 113.11, 113.08, 129.72, 129.71, 129.53, 129.51, 128.22, 126.84, 126.82, 124.03, 123.71, 123.66, 121.20, 120.95, 120.84, 120.57, 120.56, 34.11, 29.14, 26.16, 24.00, 22.32 ppm. UV-vis (CH$_2$Cl$_2$), $\lambda_{max}$/nm (log $\varepsilon$) = 234 (4.89), 269 (4.68), 437 (4.19), 522 (4.50), 560 (4.67). FT-IR (KBr) $v =$ 2963, 1708 (C=O imide), 1673 (C=O imide), 1594, 1510, 1475, 1423, 1407, 1339, 1312, 1280, 1209, 1188, 1021, 877, 804, 705 cm$^{-1}$. MALDI-TOF MS (DCTB): m/z = 1084 [M$^+$] Calcd for C$_{66}$H$_{48}$N$_6$O$_{10}$·2H$_2$O: C, 70.70; H, 4.67; N, 7.50. Found: C, 70.44, H, 4.58, N, 7.50.
Synthesis of PBI-4

Perylene derivative 3a (100 mg, 0.092 mmol), diisopropylcarbodiimide (DIC, 15 µL, 0.097 mmol) and 1-hydroxybenzotriazole (HOBt, 13.1 mg, 0.097) were were stirred in CHCl₃ (5 mL) for 20 min. 17α-[2'(4'-'aminomethyl)phenyl]ethynylestra-1,3,5(10)-triene-3,17β-diol hydrochloride² (41.7 mg, 0.095 mmol) and pyridine (12.9 µL, 0.16 mmol) was dissolved in 5 mL of DMF and this solution was added to the reaction mixture and stirred at rt under argon for 48 h. After that, CHCl₃ was evaporated and the residue was poured into water to remove DMF. The red precipitate was filtered off and repeatedly washed with water. The product was purified by flash chromatography (SiO₂, CH₂Cl₂/MeOH 9:1), yielding 93.1 mg (70 %) of 4 as a red solid. M.p. 258 ºC.

¹H NMR (300 MHz, CDCl₃): δ = 8.38 (broad, 4H, H-pyridine), 8.31 (broad, 4H, H-pyridine), 8.26 (s, 2H, 2xH-PDI), 8.21 (s, 2H, 2xH-PDI), 7.45 (t, 1H, J=7.5 Hz, H-Ar), 7.38 (d, 2H, J=8.2 Hz, 2xH-Ar'), 7.39-7.16 (m, 14H, 8xH-pyridine and 6xAr-H), 7.13 (d, 2H, J=8.2 Hz, 2xH-Ar'), 7.10 (broad, 1H, 1xAr estradiol), 6.54 (broad, 2H, 2xAr estradiol), 5.76 (t, 1H, J=5.6 Hz, -CONH-), 4.41 (d, 2H, J=5.6 Hz, -NH-CH₂), 2.91-2.55 (m, 6H, Ar -CH₂- and 2xC(CH₃)₂), 2.48-1.22 (m, 17H, C(CH₂)-CONH- and Ar-CH₂-C(CH₂)-CONH- and 13xestradiol), 1.12 (d, 12H, J=6.9 Hz, 4xCH-(CH₃)₂), 0.92 ppm (s, 3H, CH₃estradiol). ¹³C NMR (75 MHz, CDCl₃): δ = 172.41, 162.83, 162.62, 155.11, 155.03, 152.03, 145.85, 145.81, 145.52, 142.24, 141.50, 141.46, 138.54, 138.13, 133.08, 133.06, 132.46, 131.91, 131.77, 130.06, 129.72, 129.49, 128.25, 127.66, 126.79, 126.73, 126.38, 124.68, 124.54, 124.04, 123.71, 123.68, 122.16, 121.24, 120.98, 120.87, 120.85, 120.68, 120.59, 115.59, 112.87, 93.13, 85.44, 80.20, 49.80, 47.69, 43.75, 43.21, 39.50, 39.01, 35.57, 34.68, 33.11, 29.72, 29.15, 27.26, 26.73, 26.50, 24.01, 22.91, 12.92 ppm. UVI vis (CH₂Cl₂), λmax/nm (log ε) = 233 (4.98), 260 (4.81), 279 (4.74), 437 (4.17), 522 (4.47), 559 (4.66). FT-IR (KBr) ν = 3306 (-OH), 2928, 2868, 1708 (C=O imide), 1672 (C=O imide), 1593, 1509, 1474, 1422, 1407, 1339, 1311, 1281, 1209, 1188, 1020, 877, 804, 705 cm⁻¹. ESI-MS (0.1% formic acid in acetonitrile): m/z = 1450.6 [M-H₂O+H]+, 1468 [M+H]+. Calcd for C₉₃H₇₇N₇O₁₁.3H₂O: C, 73.36; H, 5.49; N, 6.44. Found: C, 73.28, H, 5.48, N, 6.50.
Synthesis of PBI-5

To a mixture of PBI-4 (15 mg, 0.01 mmol) and p-toluenesulfonic acid (8.16 mg, 0.042 mmol) in dry THF (5 mL), DMF (0.5 mL) and dihydropyran (0.5 mL) were added and refluxed with vigorous stirring under argon for 24 h. After being cooled to rt. Et3N (0.2 mL) was added to the reaction. The residue was extracted using CH2Cl2 and washed three times with 2 M NaHCO3. The product was purified by flash chromatography (neutral alumina, CH2Cl2/acetone 20:4), yielding 4.7 mg (30 %) of 5 as a red solid. M.p. 226 ºC.

1H NMR (300 MHz, CDCl3): δ = 8.38 (broad, 4H, H-pyridine), 8.32 (broad, 4H, H-pyridine), 8.26 (s, 2H, 2xH-PDI), 8.23 (s, 2H, 2xH-PDI), 7.45 (t, 1H, J=7.5 Hz, H-Ar), 7.31 (d, 2H, J=8.2 Hz, 2xH-Ar’), 7.32-7.10 (m, 17H, 8xH-pyridine and 8xAr-H and 1xAr estradiol), 6.83 (broad d, 1H, Ar estradiol), 6.77 (broad s, 1H, Ar estradiol), 5.66 (t, 1H, J=5.6 Hz, -CONH-), 5.37 (m, 1H, THP), 5.26 (m, 1H, THP), 4.42 (d, 2H, J=5.6 Hz, -NH-CH2-Ar), 3.92 (m, 2H, THP), 3.55 (m, 2H, THP), 2.83 (m, 2H, estradiol), 2.74 (t, 2H, J=7.2 Hz, Ar-CH2-), 2.67 (sept, 2H, J=6.9 Hz, 2xCH-(CH3)2), 2.12-1.35 (m, 25H, Ar-CH2-Ar’ -CH2-CONH- and 11xestradiol and 12xTHP) 1.12 (d,12H, J=6.9 Hz, 4xCH-(CH3)2), 0.96 and 0.95 ppm (2s, 3H, CH3estradiol). 13C NMR (75 MHz, CDCl3): δ = 172.33, 162.91, 162.73, 155.29, 155.15, 148.78, 145.95, 145.89, 145.58, 142.32, 141.68, 141.59, 139.16, 138.40, 133.72, 133.36, 131.88, 131.72, 130.12, 129.83, 129.75, 129.52, 128.89, 128.64, 128.60, 127.74, 126.79, 126.30, 125.17, 124.68, 124.09, 123.98, 123.71, 121.15, 121.03, 120.89, 120.83, 120.65, 120.59, 120.48, 115.80, 113.93, 96.07, 86.03, 85.68, 61.97, 48.75, 48.61, 43.83, 43.33, 39.17, 37.30, 35.73, 34.81, 32.29, 30.93, 30.47, 29.86, 29.78, 29.20, 29.18, 26.80, 26.74, 25.31, 24.01, 23.30, 22.49, 13.36 ppm. UV-vis (CH2Cl2), λmax/nm (logε) = 233 (4.94), 260 (4.75), 278 (4.65), 438 (4.12), 522 (4.42), 559 (4.60). FT-IR (KBr) ν = 2931, 2868, 1708 (C=O imide), 1674 (C=O imide), 1594, 1509, 1474, 1422, 1407, 1339, 1311, 1281, 1208, 1188, 1020, 876, 804, 706 cm⁻¹. ESI-MS (0.1% formic acid in acetone): m/z = 1450 [M-H2O-2xTHP+H]+, 1468 [M-2xTHP+H]+, 1637 [M+H]+. Calcd for C103H93N7O13.4H2O: C, 72.39; H, 5.96; N, 5.74. Found: C, 72.70, H, 6.40, N, 5.35.
**Synthesis of PBI-5a**

Perylene 5 (3.2 mg, 0.0019 mmol) was dissolved in dry THF (2.5 mL) into a pressure flask, and MeI (2.5 mL) was added to the solution. The reaction was stirred at 80 °C under argon for 18 h. After being cooled to rt, the obtained red precipitate was filtered off and repeatedly washed with CH₂Cl₂. Methylation of pyridine groups was monitored by NMR: M.p. > 300 °C.

\[ \begin{align*}
\text{1H NMR (300 MHz, CD}_3\text{OD): } & \delta = 9.15 \text{ (broad s, 2H, 2xH-pyridinium),} \\
& 9.06 \text{ (broad s, 2H, 2xH-pyridinium'),} \\
& 8.68 \text{ (m, 4H, 4xH-pyridinium),} \\
& 8.45 \text{ (s, 2H, 2xH-PDI),} \\
& 8.41 \text{ (s, 2H, 2xH-PDI),} \\
& 8.43-8.32 \text{ (m, 4H, 4xH-pyridinium),} \\
& 8.03 \text{ (m, 4H, 4xH-pyridinium),} \\
& 7.46 \text{ (t, 1H, J=7.5 Hz, H-Ar),} \\
& 7.38 \text{ (d, 2H, J=8.0 Hz, 2xH-Ar'),} \\
& 7.32 \text{ (d, 2H, J=7.5 Hz, H-Ar),} \\
& 7.31 \text{ (d, 2H, J=7.9 Hz, 2xH-Ar''),} \\
& 7.26 \text{ (d, 2H, J=7.9 Hz, 2xH-Ar'''),} \\
& 7.21 \text{ (d, 2H, J=8.0 Hz, 2xH-Ar'''),} \\
& 7.06 \text{ (d, 1H, J=9 Hz, Ar\text{estradiol},} \\
& 6.47 \text{ (d, 1H, J=9 Hz, Ar\text{estradiol'),} \\
& 6.39 \text{ (s, 1H, Ar\text{estradiol),} \\
& 5.17 \text{ (t, 1H, J=5.6 Hz, -CONH-),} \\
& 5.00-4.70 \text{ (m, 2H, 2xTHP),} \\
& 4.41 \text{ (s, 6H, 6xCH\text{3pyridinium},} \\
& 4.40 \text{ (s, 6H, 6xCH\text{3pyridinium'),} \\
& 4.35 \text{ (broad, 2H, -NH-C\text{2-H}_2-Ar),} \\
& 3.84 \text{ (m, 1H, THP),} \\
& 3.64 \text{ (m, 1H, THP),} \\
& 3.54 \text{ (m, 1H, THP),} \\
& 3.44 \text{ (m, 1H, THP),} \\
& 2.87-2.62 \text{ (m, 6H, 2xestradiol and 2xAr-C\text{2-H}_2-C\text{2-H}_2-(CH\text{3})_2,} \\
& 2.35 \text{ (m, 2H, estradiol),} \\
& 2.31 \text{ (t, 2H, J=6.9 Hz, C\text{2-H}_2-C\text{2-H}_2-(CH\text{3})_2,} \\
& 2.20-1.26 \text{ (m, 25H, Ar-C\text{2-H}_2-C\text{2-H}_2-C\text{2-H}_2-(CH\text{3})_2,} \\
& 1.09 \text{ (d, 12H, J=6.9 Hz, 4xCH-(CH\text{3})_2,} \\
& 0.90 \text{ ppm (broad s, 3H, CH\text{3estradiol).} }
\end{align*} \]
Synthesis of PBI-5b

PBI-5a and HCl 37% (0.5 mL) in MeOH (4mL) were stirred at rt under argon atmosphere during 24 h. The solvent was evaporated and the product was poured into ethyl ether. The obtained brown precipitate was filtered off and was repeatedly centrifuged with CH2Cl2/ethyl ether. The red solid was vacuum dried. Alcohol deprotection was monitored by NMR: M.p. > 300 ºC.

1H NMR (300 MHz, DMSO-d6): δ = 9.23 (broad s, 2H, 2xH-pyridinium), 9.20 (broad s, 2H, 2xH-pyridinium), 8.85 (m, 4H, 4xH-pyridinium), 8.43 (s, 2H, 2xH-PDI), 8.36 (s, 2H, 2xH-PDI), 8.3 (m, 4H, 4xH-pyridinium), 8.08 (m, 4H, 4xH-pyridinium), 7.46 (t, 1H, J=7.5 Hz, H-Ar), 7.40 (d, 2H, J=8.0 Hz, 2xH-Ar), 7.37-7.19 (m, 8H, 2xH-Ar and 2xH-Ar and 4xH-Ar), 7.03 (d, 1H, J=9 Hz, Ar-estradiol), 6.50 (d, 1H, J=9 Hz, Ar-estradiol), 6.46 (s, 1H, Ar-estradiol), 6.13 (t, 1H, -CONH-), 4.36 (s, 6H, 6xCH3pyridinium), 4.33 (s, 6H, 6xCH3pyridinium), 4.29 (broad, 2H, -NH-CH2-Ar), 2.83-2.58 (m, 6H, 2xestradiol and 2xAr-CH2- and 2xCH3(CH3)2), 2.39-2.12 (m, 4H, 2xestradiol and CH2-CNONH-), 2.00-1.20 (m, 13H, Ar-CH2-CH2-CH2-CNONH- and 11xestradiol), 1.04 (d, 12H, J=6.7 Hz, 4xCH-(CH3)2), 0.87 ppm (broad s, 3H, CH3estradiol).
**Synthesis of PBI-1**

PBI-5b (2 mg, 0.0012 mmol) and silver methanesulfonate (0.98 mg, 0.0048 mmol) were added to methanol (5 mL) to form a white precipitate (silver iodide), which was removed by filtration to give a clear red solution. MeOH was evaporated and the product was centrifuged several times in CH₂Cl₂. 1 as red solid (3 mg, 80%) was obtained after evaporation of solvent. The pure product was obtained without further purification method. M.p. > 300 ºC.

¹H NMR (300 MHz, CD₃OD): δ = 9.03 (broad, 2H, 2xH-pyridinium), 8.98 (broad s, 2H, 2xH-pyridinium'), 8.73 (broad, 4H,4x H-pyridinium), 8.46 (s, 2H, 2xH-PDI), 8.45 (s, 2H, 2xH-PDI), 8.42-8.25 (m, 4H, 4x-pyridinium), 8.03 (m, 4H, 4x-pyridinium), 7.52-7.15 (m, 11H, 3xH-Ar and 4xH-Ar' and 4xH-Ar''), 7.07 (broad, 1H, Ar₂estradiol), 6.44 (broad, 2H, Ar₂estradiol), 5.17 (broad t, 1H, -CONH-), 4.41 (s, 6H, 6xCH₃pyridinium), 4.40 (s, 6H, 6xCH₃pyridinium'), 4.36 (broad, 2H, -NH-CH₂-Ar), 2.83-2.60 (m, 6H, 2xestradiol and 2xA _r-CH₂- and 2xC_H-(CH₃)₂), 2.66 (s, 12H, SO₃-CH₃), 2.31 (m, 4H, 2xestradiol and CH₂CONH-), 2.11-1.25 (m, 13H, Ar-CH₂-C_H₂-CH₂-CONH- and 11xestradiol), 1.09 (d, 12H, J=6.5 Hz, 4xCH- (CH₃)₂), 0.90 ppm (s, 3H, CH₃estradiol). ¹³C NMR (75 MHz, CD₃OD): δ = 175.33, 164.10, 164.07, 157.45, 157.23, 155.80, 154.90, 154.73, 147.02, 142.93, 142.74, 142.50, 142.48, 140.60, 139.26, 139.05, 138.80, 138.52, 136.70, 135.80, 135.68, 134.20, 134.08, 133.91, 133.15, 132.40, 131.50, 130.43, 130.20, 129.75, 129.55, 127.35, 127.30, 126.10, 125.60, 125.31, 125.15, 125.10, 123.81, 123.50, 116.52, 114.01, 96.02, 86.15, 81.13, 78.96, 29.34, 23.15, 13.76 ppm. UV-vis (DMSO), λmax/nm (log ε) = 273 (4.62), 418 (3.86), 505 (4.18), 539 (4.33). FT-IR (KBr) ν = 3439, 2933, 1706 (C=O imide), 1666 (C=O imide), 1597, 1501, 1409, 1384, 1338, 1273, 1200, 1074, 789, 567, 535 cm⁻¹. ESI-MS (methanol): m/z = 382 [M-4xSO₃CH₃]⁺, 541 [M-3xSO₃CH₃]²⁺, 858 [M-2xSO₃CH₃]⁻. ESI-HRMS (methanol): calculated for C₉₈H₉₂N₇O₁₄S⁺, 540.8852; found, 540.8802.
Synthesis of PBI-2

Synthesis of PBI-3b

The tetrapyridyloxiperylenebisimide 3 (50 mg, 0.046 mmol) was dissolved in dry THF (5 mL) into a pressure flask, and MeI (5 mL) was added to the solution. The reaction was stirred at 80 °C under argon for 18 h. After being cooled to rt, the obtained red precipitate was filtered off and repeatedly washed with CH₂Cl₂. Methylation of pyridine groups was monitored by NMR:

¹H NMR (300 MHz, CD₃OD): δ = 9.11 (broad s, 2H, 2xH-pyridinium), 9.00 (broad s, 2H, 2xH-pyridinium’), 8.88 (m, 4H, 4x H-pyridinium), 8.46 (s, 2H, 2xH-PDI), 8.41 (s, 2H, 2xH-PDI), 8.45-8.31 (m, 4H, 4xH-pyridinium), 8.04 (d, 2H, J=6.0 Hz, 2xH-pyridinium), 8.01 (d, 2H, J=6.0 Hz, 2xH-pyridinium’), 7.45 (t, 1H, J=7.5 Hz, H-Ar), 7.35 (d, 2H, J=8.0 Hz, 2xH-Ar’), 7.31 (d, 2H, J=8.0 Hz, H-Ar), 7.25 (d, 2H, J=8.0 Hz, 2xH-Ar’’), 4.41 (s, 6H, 6xCH₃pyridinium), 4.39 (s, 6H, 6xCH₃pyridinium’), 2.82 (sept, 2H, J=6.8 Hz, 2xCH-(CH₃)₂), 2.73 (t, 2H, J=7.5 Hz, Ar-CH₂-), 2.35 (t, 2H, J=7.3 Hz, CH₂CO₂H), 1.95 (m, 2H Ar-CH₂-CH₂-CH₂-CO₂H), 1.09 (d, 12H, J=6.8 Hz, 4xCH-(CH₃)₂).
Synthesis of PBI-2

PBI-3b (65 mg, 0.039 mmol) and silver methanesulfonate (32 mg, 0.157 mmol) were added to methanol (10 mL) to form a white precipitate (silver iodide), which was removed by filtration to give a clear red solution. MeOH was evaporated and the product was centrifuged several times in CH₂Cl₂. A red solid (56 mg, 80%) was obtained after evaporation of solvent. The pure product 2 was obtained without further purification method.

¹H NMR (300 MHz, CD₃OD): δ = 9.00 (m, 4H, 4xH-pyridinium), 8.72 (broad, 4H, 4xH-pyridinium), 8.45 (s, 2H, 2xH-PDI), 8.40 (s, 2H, 2xH-PDI), 8.33 (m, 4H, 4xH-pyridinium), 8.03 (m, 4H, 4xH-pyridinium), 7.64 (t, 1H, J=7.5 Hz, H-Ar), 7.43-7.18 (m, 12H, 8xH-pyridine and 2xAr-H and 2xAr-H'), 7.15 (d, 2H, J=8.0 Hz, 2xH-Ar'), 4.40 (broad s, 12H, CH₃pyridinium), 2.71 (m, 4H, Ar-CH₂- and 2xCH-(CH₃)₂), 2.67 (s, 12H, SO₃-CH₃), 2.39 (m, 2H, CH₂-CO₂H), 1.99 (m, 2H Ar-CH₂-CH₂-CO₂H), 1.09 ppm (d, 12H, J=6.5 Hz, 4xCH-(CH₃)₂). ¹³C NMR (75 MHz, CD₃OD): δ = 177.24, 164.18, 164.15, 157.47, 157.10, 154.70, 154.53, 147.14, 147.12, 142.90, 142.70, 142.48, 142.44, 140.57, 139.25, 139.03, 138.97, 135.80, 135.67, 135.65, 134.02, 133.99, 131.48, 130.41, 130.22, 129.81, 129.80, 127.27, 126.05, 125.34, 125.19, 125.17, 123.80, 123.48, 39.58, 35.80, 34.16, 30.31, 27.84, 24.34 ppm. UV/Vis (DMSO), λmax/nm (log ε) = 274 (4.70), 413 (3.99), 540 (4.25), 440 (4.38). FT-IR (KBr) ν = 3435, 2963, 1705 (C=O imide), 1667 (C=O imide), 1596, 1501, 1409, 1339, 1274, 1198, 1109, 1076, 1060, 790, 971, 617, 567, 534 cm⁻¹. ESI-MS (methanol): m/z = 286 [M-4xSO₃CH₃]⁺, 413 [M-3xSO₃CH₃]²⁺, 667 [M-2xSO₃CH₃]³⁺. ESI-HRMS (methanol): calculated for C₇₂H₆₆N₆O₁₆S₂⁺², 667.1983; found, 667.2062.
$^1$H- $^{13}$C-NMR and MS spectra of characterized compounds.
Figure 1. $^1$H-NMR Monitoring to check tetramethylation, deprotection and anion exchange reactions yielding 1. Black arrows indicate the protons of the THP groups, red arrows indicate CH$_3$-piridinium protons, and blue arrow indicates the protons of CH$_3$-SO$_3^-$. 

Electronic Supplementary Material (ESI) for Chemical Communications
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Materials and methods for the biological experiments.

**MCF7 cells culture and Islet cells isolation**
The breast cancer cell line, MCF7, is maintained in culture in Dulbecco’s Modified Eagle’s Medium (Sigma, Madrid, Spain) supplemented with NaHCO$_3$ 3.7g/L, 10% inactivated fetal bovine serum, 200 U/mL penicillin, 0.2 mg/mL streptomycin penicillin and 2 mM L-glutamine. One day before the experiment, around 150000 cells were plated in 12 mm covers. Pancreatic islets of Langerhans were isolated by collagenase (Sigma, Madrid, Spain) digestion as previously described. Islets were dispersed into single cells with trypsin. Cells were then centrifuged and resuspended in RPMI 1640 without phenol-red (Invitrogen, Barcelona) and with 10% charcoal dextran treated fetal bovine serum (Hyclone, USA), 2 mM L-glutamine, 200 U/mL penicillin and 0.2 mg/mL streptomycin. Cells were then plated on coverslips and used within 24 hours of culture.

**Cell labeling and immunocytochemistry**
Cells were fixed with Bouin (Sigma, Madrid, Spain) for 2 min and then permeabilized with 0.1% Triton X-100, 5 min. For the immunostaining with the antibody against the estrogen receptor alpha ($\text{ER}_\alpha$), cells were fixed for 20 min with Bouin and then permeabilized for 15 min. Cells were then pretreated with 5% bovine serum albumin (BSA) for 1 h at room temperature, to block non-specific staining. Afterwards, the different perylenes, namely 1 and 2, were added to the cells in PBS with 1% BSA and incubated overnight at 4 °C. After this, cells were washed several times with PBS, left to dry and mounted using Prolong® Gold Antifade Reagent (Invitrogen, Barcelona, Spain). For the $\text{ER}_\alpha$ immunostaining, the anti-$\text{ER}_\alpha$ G-20 was used at 1:100 (sc-544, Santa Cruz), followed by incubation with a secondary antibody anti-rabbit 488 (1:500, Alexa FluorR, Invitrogen). Images were obtained using a confocal Zeiss Pascal 5 microscope with Zeiss 40X and 63X objectives (numerical aperture=1.3 and 1.25 respectively). Images were analyzed using the LSM Zeiss software (Zeiss, Jena, Germany). Perylene molecules were excited using the 488nm laser line and emitted light was collected using a long-pass filter LP530.
References.

(1) Kohl, C.; Qu, J.; Müllen, K. WO 2004/076563 A1