Supporting Information

Synthesis of flexible tetrapyridylethane from pyridylpyrylium dications

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1- General experimental details

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk-line Techniques. Infrared-spectra were recorded on a Perkin-Elmer spectrum1000 FTIR using KBr plates. All NMR data are reported in ppm (δ) relative to tetramethylsilane as external reference. Coupling constants are reported in Hz. 1H and 13C NMR chemical shift assignments are supported by data obtained from 1H-1H cosy, 1H-13C HMQC and 1H-13C HMBC. Spectra were recorded at room temperature in CDCl₃ on a Bruker DRX 500 spectrometer and a Bruker Advance 300 spectrometer at the “Institut Universitaire de Technologie de Lannion”. Mass spectra or elemental analyses were performed at the “Centre Régional de Mesures Physiques de l’Ouest” (CRMPO, University of Rennes). Microanalytical data were obtained with a Thermo-Finnigan Flasch EA 1112 CHNS/0 analyzer. Mass spectra were obtained with a high resolution MS/MS Zab spectra Tof micromass. ESR spectra of toluenic solution were recorded at 293K in a glass capillary using a Brücker Elexsys E 500 spectrometer with 100 KHz modulation. UV-vis absorption spectra were recorded on a UV-vis Perkin Elmer spectrophotometer lambda 25. Emission measurements were performed using a JYB fluoromax-4 spectrofluorimeter at 25°C. Quantum yield was determined using the corrected emission quantum yield of a coumarin 317 standard. The electrochemical studies of the compounds were performed in a glovebox (Jacomex) (O₂ < 1 ppm, H₂O < 1 ppm) with a home-designed 3-electrodes cell (WE: Pt, RE: Ag wire, CE: Pt). Ferrocene was added at the end of each experiment to determine redox potential values. The potential of the cell was controlled by an AUTOLAB PGSTAT 100 (Ecochemie) potentiotstat monitored by a computer. Anhydrous “extra-dry” dichloromethane (H₂O < 30 ppm, Acros) was used as received and kept under N₂ in the glovebox. The supporting salt NBu₄PF₆ was synthesized from NBu₄OH (Fluka) and HPF₆ (Aldrich). It was then purified, dried under vacuum for 48 hours at 100°C, then kept under N₂ in the glovebox. Single crystal of 4c was mounted on a glass fiber with oil and measured on a Nonius four circle diffractometer equipped with a CCD camera and a graphite monochromated MoKα radiation source (λ = 0.71073 Å), from the Centre de Diffractométrie (CDFIX), Université de Rennes 1, France. Data were collected at 293 K. Structures were solved by the direct method using SIR97 and refined by a full matrix least-squares procedure based on F² with SHELXL2013. Hydrogen atoms were fixed into idealized positions (riding model) and assigned temperature factors Hiso (H).

2- General procedure

2-1 synthesis of compounds 1

2-[4-(2,6-Diphenyl-pyran-4-ylidenemethyl)-phenyl]-pyridine 1a

Small excess of n-butyllithium 2.5 M in hexanes (0.70 mL, 1.75 mmol, 1.1 equiv.) was added dropwise at -78 °C, under a nitrogen atmosphere, to a degassed solution of 2,6-diphenyl-4H-pyran-4-yl tributylphosphonium tetrafluoroborate salt (1g, 1.67 mmol, 1 equiv.) in dry THF
(15 mL). After 15 min, the 4-(2-pyridylbenzaldehyde) (295 mg, 1.60 mmol, 0.95 equiv.) was added. The solution was stirred at -78°C for 30 min, and allowed to warm to room temperature for 2 h. THF was evaporated and the residue dissolved in a mixture of CH₂Cl₂/water 1:1 (30 mL) and the organic layer separated. The aqueous layer was extracted with CH₂Cl₂ (2 x 15 mL). The combined organic extracts were dried with MgSO₄ and the solvents evaporated. The crude product was obtained by crystallization in a diethylether/dichloromethane (80/20) solution (515 mg, 77%) as a yellow solid. mp : 188-190°C ¹H NMR (500 MHz, CDCl₃) δ(ppm) 6.01 (s, 1H), 6.44 (d, 1H, J = 2.0 Hz), 7.08 (d, 1H, J = 2.0 Hz), 7.24 (dd, 1H, J = 4.5 Hz, J = 4.4 Hz) 7.42-7.48 (m, 6H), 7.52 (d, 2H, J = 8.2 Hz), 7.78-7.81 (m, 6H, 4H(ph)+2H (pyridine)), 8.03 (d, 2H, J = 8.2 Hz), 8.72 (d, 1H, J = 2.5 Hz) ; ¹³C NMR and JMOD (125 MHz, CDCl₃) δ (ppm) 157.1(C), 152.8(C), 151.0(C), 149.7(CH), 139.4(C), 136.8(CH), 135.0(C), 133.4(C), 133.3(C), 130.9(CH), 130.1(C), 129.3(CH), 129.1(CH), 128.6(CH), 128.1(CH), 127.0(CH), 124.9 (CH), 124.6(CH), 121.8(CH), 120.2(CH) 113.7 (CH), 108.6 (CH), 102.2 (CH). HRMS (ESI) m/z calculated for C₂₉H₂₂NO [M+H]+ 400.17014, found 400.1699. IR ν(cm⁻¹) = 3049; 2958; 1722; 1655; 760.

3-[4-(2,6-Diphenyl-pyran-4-ylidenemethyl)-phenyl]-pyridine 1b

Small excess of n-butyllithium 2.5 M in hexanes (0.8 mL, 1.92 mmol, 1 equiv.) was added dropwise at -78 °C, under a nitrogen atmosphere, to a degassed solution of 2,6-diphenyl-4H-pyran-4-yl tributylphosphonium tetrafluoroborate salt (1.2 g, 2 mmol, 1 equiv.) in dry THF (15 mL). After 15 min, the 4-(3-pyridylbenzaldehyde) (350 mg, 1.9 mmol, 0.95 equiv.) was added. The solution was stirred at -78°C for 30 min, and allowed to warm to room temperature for 2 h. THF was evaporated and the residue dissolved in a mixture of CH₂Cl₂/water 1:1 (30 mL) and the organic layer separated. The aqueous layer was extracted with CH₂Cl₂ (2 x 15 mL). The combined organic extracts were dried with MgSO₄ and the solvents evaporated. The crude product was obtained after silicagel chromatography (diethylether/ethyl acetate : 80/20) and crystallization in a diethylether/dichloromethane (80/20) solution (600 mg, 71%) as a yellow solid. mp : 188-190°C ¹H NMR (500 MHz, CDCl₃) δ(ppm) 6.08 (s, 1H), 6.73 (d, 1H, J = 2.0 Hz), 7.17 (d, 1H, J = 2.0 Hz), 7.40-7.52 (m, 7H, 6H(ph)+ 1H(pyridine)), 7.60 (d, 2H, J = 8.0 Hz), 7.72 (d, 2H, J = 8.0 Hz), 7.89-7.92 (m, 4H), 8.05 (d, 1H, J = 10.0 Hz), 8.55 (d, 1H, J = 6 Hz), 8.91 (d, 1H, J = 2.5 Hz) ; ¹³C NMR and JMOD (125 MHz, CDCl₃) δ (ppm) 153.1(C), 151.2(C), 146.9(CH), 144.3(CH), 139.0(C), 135.1(CH), 133.4(C), 130.3(CH), 129.5(CH), 128.8(CH), 127.1(CH), 124.9(CH), 124.5(CH),
123.9(CH), 113.2(CH), 108.5(CH), 102.0(CH). HRMS (ESI) m/z calculated for C_{29}H_{22}NO [M+H]^+ 400.1696, found 400.16959. m/z calculated for C_{29}H_{21}NO M^+. 399.16176, found 399.1616. Elemental analysis for C_{29}H_{21}NO Calc.C 87.19 H 5.30 N 3.51, found C 87.07 H 5.28 N 3.61. IR ν (cm⁻¹) = 3051; 2972; 1654; 1588; 860.

4-[4-(2,6-Diphenyl-pyran-4-ylidenemethyl)-phenyl]-pyridine 1c

Small excess of n-butyllithium 2.5 M in hexanes (0.66 mL, 1.65 mmol, 1.1 equiv.) was added dropwise at -78 °C, under a nitrogen atmosphere, to a degassed solution of 2,6-diphenyl-4H-pyran-4-yl tributylphosphonium tetrafluoroborate salt (975mg, 1.63 mmol, 1 equiv.) in dry THF (15 mL). After 15 min, the 4-(4-pyridylbenzaldehyde) (300 mg, 1.6 mmol, 1 equiv.) was added. The solution was stirred at -78°C for 30 min, and allowed to warm to room temperature for 2h. THF was evaporated and the residue dissolved in a mixture of CH₂Cl₂/water 1:1 (30 mL) and the organic layer separated. The aqueous layer was extracted with CH₂Cl₂ (2 x 15 mL). The combined organic extracts were dried with MgSO₄ and the solvents evaporated. The crude product was obtained by crystallization in a diethylether/dichloromethane (80/20) solution (620 mg, 96%) as a yellow solid. mp: 191-193°C. H NMR (500 MHz, CDCl₃) δ (ppm) 5.97 (s, 1H), 6.45 (d, 1H, J = 2.0 Hz), 7.04 (d, 1H, J = 2.0 Hz), 7.41-7.47 (m, 6H), 7.51 (d, 2H, J = 8.0 Hz), 7.54 (d, 2H, J = 5.5 Hz), 7.66 (d, 2H, J = 8.0 Hz), 7.78 (m, 4H), 8.66 (d, 2H, J = 5.5 Hz); ¹³C NMR and JMOD (125 MHz, CDCl₃) δ (ppm) 153.2(C), 151.2(C), 150.32(CH), 150.35(CH), 147.9(C), 139.7(C), 134.7(C), 133.4(C), 133.2(C), 130.4(C), 129.5(CH), 129.2(CH), 128.7(CH), 128.4(CH), 127.1(CH), 125.0(CH), 124.6(CH), 121.1(CH), 113.2(CH), 108.6(CH), 102.0(CH). HRMS (ESI) m/z calculated for C_{29}H_{22}NO [M+H]^+ 400.17014, found 400.1700. Elemental analysis for C_{29}H_{21}NO Calc.C 87.19 H 5.30 N 3.51, found C 86.2 H 5.21 N 3.53. IR ν(cm⁻¹) = 3053; 2880; 1655; 1591; 1579; 1448; 1277; 1070; 944; 914; 868.

2-2 synthesis of compound 2a

4,4’-(1,2-bis(4-(pyridin-2-yl)phenyl)ethane-1,2-diyl)bis(2,6-diphenylpyrylium) 2a

AgBF₄ (78 mg, 0.4 mmol) was added to a solution of compound 1a (160 mg, 0.4 mmol) in 10mL of methylene chloride. The green mixture obtained was stirred 2h at room temperature.
After this time, the formation of a green precipitate and a metallic residue of Ag was observed. After addition of 50 mL of methylene chloride, the mixture was filtered to eliminate Ag residue. The solution obtained was concentrated to 10 mL by solvent evaporation and 30 mL of diethylether were added. After 24h at -18°C the crude product 2a was obtained by filtration as a green powder. 180 mg (46% yield) of compound 2a was obtained as a mixture of two diastereoisomers (60% Maj / 40% Min) after recrystallization of the product in diethylether /CH₂Cl₂ (20/80). Due to the low solubility of this compound in acetone d₆ or CD₂Cl₂, 2D (HMQC) investigation were performed to determine ¹³C chemical shifts instead of usual ¹³C or Jmod analysis. ¹H NMR (500 MHz, acetone d₆) δ/ppm 6.51 (s, 2H, Maj), 6.55 (s, 2H, Min), 7.26-7.60 (m, 16H, Min), 7.70-7.87 (m, 16H, Maj), 7.98 (m, 6H, Min), 8.08 (m, 6H, Maj), 8.12 (d, 4H, J = 8 Hz, Min), 8.18 (d, 4H, J = 10 Hz, Maj), 8.31 (d, 4H, J = 10 Hz, Min), 8.51 (m, 10H, Min + Maj), 8.65 (d, 2H, J = 4 Hz, Min), 8.74 (d, 2H, J = 4 Hz, Maj), 9.17 (s, 4H, Min), 9.32 (s, 4H, Maj). 2D HMQC (500 MHz/125MHz, acetone d₆) δ/ppm, major isomer) 147.0, 136.9, 131.1, 130.5, 130.0, 129.8, 129.6, 129.5, 119.0, 54.1. δ/ppm, minor isomer) 147.5, 130.5, 130.2, 129.0, 125.5, 122.1, 118.9, 54.1. HRMS (ESI) m/z calculated for C₂₉H₂₁NO[A]⁺ 399.16176, found 399.1619. m/z calculated for C₅₈H₄₀N₂O₂ M⁴⁺: 796.30843, found 796.3079. IR ν/cm⁻¹) = 3065 ; 1619 ; 1508 ; 1466 ; 1438 ; 1059 ; 1021, 779 ; 680.

2-3 synthesis of compounds 3

Compound 1a, 1b or 1c and AgBF₄ were stirred in degassed solution of methylene chloride (10mL) at room temperature for 6h. The initial yellow solution became green and we observed apparition of a green precipitate. A pH=9 (glycine buffer) was then added to the solution and the heterogeneous mixture was stirred half an hour. Ag residue was then eliminated by filtration and the organic layer was extracted 3 times with diethylether and washed 3 times with water. The extract was dried over MgSO₄. After evaporation of the solvent, the crude product was obtained without other purification as red powder.

1,2-bis(2,6-diphenyl-4H-pyran-4-ylidene)-1,2-bis(4-(pyridin-2-yl)phenyl)ethane 3a

Compound 1a (380mg, 0.95mmol) react with AgBF₄ (185mg, 1 eq). Compound 3a was obtained as red powder (280 mg, 73% yield). mp : 275-277°C. ¹H NMR (500 MHz, CDCl₃) δ/ppm 6.66 (s, 2H), 7.06 (s, 2H), 7.17 (m, 2H), 7.29-7.44 (m, 12H), 7.55 (d, 4H, J = 10.0 Hz), 7.68 (m, 8H), 7.74 (d, 4H, J = 10.0 Hz), 7.91 (d, 4H, J = 8 Hz), 8.66 (d, 2H, J = 4 Hz);
$^{13}$C NMR and JMOD (125 MHz, CDCl$_3$) $\delta$ (ppm) 157.3(C), 152.3(C), 151.4(C), 149.6(CH), 142.0(C), 137.0(C), 136.6(CH), 133.7(C), 133.6(C), 130.4(C), 129.9(CH), 129.0(CH), 128.6(CH), 128.0(C), 126.8(CH), 124.7(CH), 124.6(C), 121.8(CH), 120.3(CH), 106.4(CH), 104.7(CH). HRMS (ESI) m/z calculated for C$_{58}$H$_{41}$N$_2$O$_2$ [M+H]$^+$ 797.31625, found 797.3169.

Elemental analysis for C$_{58}$H$_{40}$N$_2$O$_2$ Calc.C 87.41 H 5.06 N 3.51, found C 86.28 H 5.75 N 3.14.

IR $\nu$(cm$^{-1}$) = 2923 ; 1649 ; 1598 ; 1584 ; 1463 ; 1273 ; 1068 ; 916 ; 762 ; 690.

1,2-bis(2,6-diphenyl-4H-pyran-4-ylidene)-1,2-bis(4-(pyridin-3-yl)phenyl)ethane 3b

Compound 1b (200 mg, 0.5mmol) react with AgBF$_4$ (100mg, 1 eq). Compound 3b was obtained as red powder (160 mg, 80%yield). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$(ppm) 6.66 (s, 2H, $J = 1.9$ Hz), 7.06 (s, 2H, $J = 2.0$ Hz), 7.33-7.50(m, 14H), 7.57 (d, 8H, $J = 2.2$ Hz), 7.70 (dd, 4H, $J = 1.8$ Hz), 7.77 (dd, 4H, $J = 8.2$ Hz, $J = 1.6$ Hz), 7.93 (dt, 2H, $J = 8.2$ Hz, $J = 1.9$ Hz), 8.57 (dd, 2H, $J = 4.9$ Hz, $J = 1.5$ Hz), 8.88 (d, 2H, $J = 2.0$ Hz); $^{13}$C NMR and JMOD (125 MHz, CDCl$_3$) $\delta$ (ppm) 152.5(C), 151.6(C), 147.6(CH), 141.2(C), 136.5(C), 135.1(C) 134.4(CH), 133.6(C), 133.5(C), 130.2(CH), 129.1(CH), 129.0(CH), 128.6(CH), 128.5(CH), 128.55(C), 126.9(CH), 124.8(CH), 124.7(CH), 123.9(C), 123.7(CH), 120.3(CH), 106.2(CH), 104.4(CH). HRMS (ESI) m/z calculated for C$_{58}$H$_{40}$N$_2$O$_2$ M$^+$ 796.30843, found 796.3092. IR $\nu$(cm$^{-1}$) = 2922 ; 1647 ; 1593 ; 1484 ; 1446 ; 1278 ; 1066 ; 912 ; 690.

1,2-bis(2,6-diphenyl-4H-pyran-4-ylidene)-1,2-bis(4-(pyridin-4-yl)phenyl)ethane 3c

Compound 1c (200 mg, 0.5mmol) react with AgBF$_4$ (100mg, 1 eq). Compound 3c was obtained as red powder (120 mg, 60%yield). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$(ppm) 6.65 (d, 2H, $J = 1.9$ Hz), 7.05 (d, 2H, $J = 1.9$ Hz), 7.35-7.41(m, 6H), 7.42-7.53 (m, 8H), 7.56 (d, 4H, $J = 6.0$ Hz), 7.60 (d, 4H, $J = 6.0$ Hz), 7.65 (m, 2H), 7.69 (m, 4H), 7.77 (d, 4H, $J = 7.5$ Hz), 8.63 (d, 4H, $J = 6.0$ Hz); $^{13}$C NMR and JMOD (125 MHz, CDCl$_3$) $\delta$ (ppm) 152.5 (C), 151.8(C), 149.3(CH), 148.6 (C), 142.5(C), 135.1(C), 133.5(C), 133.4(C), 132.2(CH), 132.0(CH), 131.9(CH), 131.8(CH), 130.2 (CH), 129.2(CH), 129.0(C), 128.6(CH), 128.5(CH), 128.4(CH), 126.9(CH), 124.7(CH), 124.6(CH), 123.6(C), 121.3(CH), 106.2(CH), 104.2(CH). HRMS (ESI) m/z calculated for C$_{58}$H$_{40}$N$_2$O$_2$ C$^{2+}$ 398.15394, found 398.1546. IR $\nu$(cm$^{-1}$) = 3055 ; 1649 ; 1585 ; 1465 ; 1278 ; 1070 ; 916 ; 782 ; 680.
2.4 synthesis of compounds 4 and 5

1,2-bis(2,6-diphenylpyridin-4-yl)-1,2-bis(4-(pyridin-2-yl)phenyl)ethane 4a and spiro compound 5

20mL (excess) of an ammonia solution 25% was added to a suspension of salt 2a (two diastereoisomers) (500mg, 0.62 mmol) in diethylether at room temperature. The mixture was stirred until we observed the lack of the solid (2h). The yellow solution was extract three times with diethylether and the combined organic extracts were washed with water and dried over MgSO₄. TLC analysis of the residue shows the existence of two major products (UV detection). These compounds were separated by silica gel chromatography (ethyl acetate/petroleumether : 30/70). The crudes products 4a (133mg, 27%) and 5 (102mg, 21%) were isolated as white crystalline powders. 4a was obtained as un sole diastereoisomer.

4a: \[ ^1H\text{NMR} (300\text{ MHz, CDCl}_3) \delta (ppm) 8.64 (d, 2H, J = 4.5 Hz), 7.97 (d, 8H, J =6.7 Hz), 7.91 (d, 4H, J = 8.5Hz), 7.71 (t, 2H, J = 7.7 Hz), 7.61 (d, 2H, J = 7.7 Hz), 7.57 (s, 4H), 7.49 (d, 4H, J = 8.1 Hz), 7.38-7.47 (m, 12H), 7.20 (t, 2H, J = 6.0 Hz), 5.1 (s, 2H). \]

13C NMR and JMOD (125 MHz, CDCl₃) δ (ppm) 157.1 (C), 155.1 (C), 149.5 (CH), 142.1 (C), 139.4 (C), 137.1 (CH), 129.0 (CH), 128.9 (CH), 128.6 (CH), 127.5 (CH), 127.1 (CH), 122.2 (CH), 120.5 (CH), 119.0 (CH), 55.6 (CH). HRMS (ASAP) m/z calculated for C₅₈H₄₃N₄ [M+H]^+ 795.34822, found 795.3487.

IR ν (cm⁻¹) = 3034 ; 1591 ; 1554 ; 1466 ; 1435 ; 1415 ; 1014 ; 774 ; 748 ; 734 ; 690.

5: \[ ^1H\text{NMR} (300\text{ MHz, CDCl}_3) \delta (ppm) 8.68 (d, 1H, J = 4.3 Hz), 8.61 (d, 1H, J = 4.3 Hz), 8.02 (d, 2H, J = 4.5 Hz, 7.3 Hz), 7.94 (d, 2H, J = 7.9 Hz), 7.83 (d, 2H, J = 8.1 Hz), 7.59-7.79 (m, 6H), 7.55 (d, 2H, 6.7 Hz), 7.38-7.50 (m, 8H), 7.35 (d, 2H, J = 7.6 Hz), 7.14-7.25 (m, 6H), 7.07 (t, 1H, J = 7.0 Hz), 5.64 (s, 1H), 5.17 (d,1H, J = 12.4 Hz), 5.00 (s,1H), 3.64 (d, 1H, J = 12.1 Hz). \]

13C NMR and JMOD (125 MHz, CDCl₃) δ (ppm) 157.6 (C), 156.4 (C), 155.1 (C), 149.8 (C), 149.7 (CH), 148.3 (C), 141.7 (C), 140.5 (C), 139.9 (C), 139.4 (C), 137.05 (CH), 134.5 (C), 134.15 (C), 130.0 (CH), 129.5 (CH), 129.3 (CH), 128.8 (CH), 128.6 (CH), 128.4 (CH), 128.3 (CH), 127.9 (CH), 127.7 (CH), 127.5 (CH), 127.4 (CH), 127.3 (CH), 126.4 (CH), 124.8 (CH), 122.1 (CH), 122.0 (CH), 120.6 (CH), 115.9 (CH), 102.0 (CH), 101.2 (CH), 70.7 (CH), 51.8 (C), 51.3 (CH). HRMS (ESI) m/z calculated for C₅₈H₄₃N₃O [M+H]^+ 796.33224, found 796.3331. IR ν (cm⁻¹) = 3055 ; 1686 ; 1587 ; 1560 ; 1495 ; 1467 ; 1435 ; 1283 ; 1060 ; 1027 ; 913 ; 777 ; 741 ; 762 ; 694.

1,2-bis(2,6-diphenylpyridin-4-yl)-1,2-bis(4-(pyridin-3-yl)phenyl)ethane 4b
AgBF$_4$ (49 mg, 0.25 mmol) was added to a solution of compound 1b (100 mg, 0.25 mmol) in 10mL of methylene chloride. The green mixture obtained was stirred 2h at room temperature. After this time, the formation of a green precipitate and a metallic residue of Ag were observed. After addition of 50 mL of methylene chloride, the mixture was filtered to eliminate Ag residue. Methylene chloride was then evaporated and 30 mL of diethylether and 20 mL of ammoniac solution (25%) were added to the obtained residue. The degassed mixture was stirred at room temperature 10 hours. We observed the formation of a yellow precipitate. After filtration, the solid was dissolved in acetone and recrystallized by addition of diethylether at low temperature (-18°C). Compound 4b was obtained as a white crystalline powder (m = 40 mg, 40%). $^1$H NMR (300 MHz, acetone $d_6$) $\delta$(ppm) 8.71 (d, 2H, $J$ = 2.1 Hz), 8.46 (d, 2H, $J$ = 4.8 Hz), 8.18 (s, 4H), 8.16 (s, 2H), 7.99 (d, 4H, $J$ = 8.3 Hz), 7.86 (dt, 4H, $J$ = 8.2 Hz, $J$ = 2.0 Hz ), 7.60 (d, 4H, $J$ = 8.2 Hz ), 7.40-7.54 (m, 14H), 7.33 (dd, 2H, $J$ = 8.0 Hz, $J$ = 4.8 Hz), 5.94 (s, 2H). $^{13}$C NMR and JMOD (125 MHz, CDCl$_3$) $\delta$(ppm) 156.7 (C), 154.4 (C), 148.4 (CH), 147.8 (CH), 142.4 (C), 139.4 (C), 136.2 (C), 135.5 (C), 133.7 (CH), 129.4 (CH), 128.9 (CH), 128.6 (CH), 127.3 (CH), 126.8 (CH), 123.4 (CH), 118.9 (CH), 54.0 (CH). HRMS (ESI) m/z calculated for C$_{58}$H$_{43}$N$_4$[M+H]$^+$ 795.34822, found 795.3479. IR $\nu$(cm$^{-1}$) = 3034 ; 2923; 1593 ; 1555 ; 1474 ; 1415 ; 1028 ; 776 ; 735 ; 692.

1,2-bis(2,6-diphenylpyridin-4-yl)-1,2-bis(4-(pyridin-4-yl)phenyl)ethane 4c

We used the exact same procedure as it followed for the synthesis of 4b. AgBF$_4$ (100 mg, 0.50 mmol) was added to a solution of compound 1c (200 mg, 0.50 mmol) in 10mL of methylene chloride. Compound 4c was obtained as a white crystalline powder (m = 100 mg, 55%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$(ppm) 8.51 (d, 4H, $J$ = 6.1 Hz), 8.18 (s, 8H), 8.16 (s, 4H), 8.01 (d, 4H, $J$ = 8.4 Hz), 7.67 (d, 4H, $J$ = 8.3 Hz), 7.43-7.53 (m, 16H), 5.97 (s, 2H). $^{13}$C NMR and JMOD (125 MHz, CDCl$_3$) $\delta$(ppm) 156.7 (C), 154.2 (C), 150.2 (CH), 146.9 (C), 139.4 (C), 137.7 (C), 136.4 (C), 129.5 (CH), 129.0 (CH), 128.6 (CH), 127.2 (CH), 126.8 (CH), 123.7 (CH), 121.0 (CH), 118.9 (CH), 54.0 (CH). HRMS (ESI) m/z calculated for C$_{58}$H$_{43}$N$_4$[M+H]$^+$ 795.34822, found 795.3480. IR $\nu$(cm$^{-1}$) = 3033 ; 1595 ; 1555 ; 1474 ; 1415 ; 1028 ; 776 ; 735 ; 693.
3. $^1H$, $^{13}C$, 2D NMR spectra

3-1 monopyrans 1

$^1H$ NMR spectrum of compound 1a in CDCl$_3$ at 293K

$^{13}C$ (Jmod) NMR spectrum of compound 1a in CDCl$_3$ at 293K
$^1$H NMR spectrum of compound 1b in acetone-$d_6$ at 293K

$^{13}$C (Jmod) NMR spectrum of compound 1b in acetone-$d_6$ at 293K
$^1$H NMR spectrum of compound 1c in CDCl$_3$ at 293K

$^{13}$C (Jmod) NMR spectrum of compound 1c in CDCl$_3$ at 293K
3-2 bispyrans 3

$^1$H NMR spectrum of compound 3c in CDCl$_3$ at 293K

$^{13}$C (Jmod) NMR spectrum of compound 3c in CDCl$_3$ at 293K
$^1$H NMR spectrum of compound 3b in CDCl$_3$ at 293K

$^{13}$C (Jmod) NMR spectrum of compound 3b in CDCl$_3$ at 293K
$^1$H NMR spectrum of compound 3a in CDCl$_3$ at 293K

$^{13}$C (Jmod) NMR spectrum of compound 3a in CDCl$_3$ at 293K
3-3 tetrapyridines 4

$^1$H NMR spectrum of compound 4c in acetone-$d_6$ at 293K

$^{13}$C (Jmod) NMR spectrum of compound 4c in acetone-$d_6$ at 293K
$^1$H NMR spectrum of compound 4a in acetone-$d_6$ at 293K

$^{13}$C (Jmod) NMR spectrum of compound 4a in acetone-$d_6$ at 293K
$^1$H NMR spectrum of compound 4b in acetone-$d_6$ at 293K

$^{13}$C (Jmod) NMR spectrum of compound 4b in acetone-$d_6$ at 293K
3-4 *pyrylium* dications 2

$^1$H NMR spectrum of compound 2a in acetone-$d_6$ at 293K

2D ($^1$H/$^{13}$C) HSQC spectrum of compound 2a in acetone-$d_6$ at 293K
\(^1\)H NMR spectrum of compound 2b in acetone-\(d_6\) at 293K
$^1$H NMR spectrum of compound 5 in acetone-$d_6$ at 293K

$^{13}$C (Jmod) NMR spectrum of compound 5 in acetone-$d_6$ at 293K
4- IR spectra of compounds 1-5
IRTF/ATR spectrum of compound 2b

IRTF/ATR spectrum of compound 3a
IRTF/ATR spectrum of compound 3b

IRTF/ATR spectrum of compound 3c
IRTF/ATR spectrum of compound 4a

IRTF/ATR spectrum of compound 4c
IRTF/ATR spectrum of compound 4b

IRTF/ATR spectrum of compound 5
5- Absorption and emission spectra of compound 2a

UV-vis (red curve) and emission (blue curve) spectra of compound 2a in CH₂Cl₂ at 25°C. Excitation at 400 nm. [2a]= 8.10⁻⁶ M. Emission intensity was normalized with the absorbance at 286 nm.

6- Crystallographic data of compound 4c

6-1 Crystal data

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₅₈H₄₂N₄</td>
</tr>
<tr>
<td>Formula weight</td>
<td>794.95</td>
</tr>
<tr>
<td>Temperature</td>
<td>293(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, Space group</td>
<td>Monoclinic, P 2/n</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>10.9142(17) Å</td>
</tr>
<tr>
<td>b</td>
<td>13.574(2) Å</td>
</tr>
<tr>
<td>c</td>
<td>14.539(2) Å</td>
</tr>
<tr>
<td>β</td>
<td>76.691(8)°</td>
</tr>
<tr>
<td>Volume</td>
<td>2096.1(5) Å</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.260 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.074 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>836</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.018 x 0.015 x 0.012 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>5.194 to 25.258°.</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-13 ≤ h ≤ 13, -16 ≤ k ≤ 16, -17 ≤ l ≤ 17</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>7210</td>
</tr>
</tbody>
</table>
Independent reflections 3743 \[R(int) = 0.1898\]
Completeness to theta = 25.242° 98.7 %
Absorption correction None
Refinement method Full-matrix least-squares on $F^2$
Data / restraints / parameters 3743 / 0 / 280
Goodness-of-fit on $F^2$ 0.935
Final R indices [I>2\sigma(I)] R1 = 0.0919, wR2 = 0.2180
R indices (all data) R1 = 0.2867, wR2 = 0.3083
Largest diff. peak and hole 0.293 and -0.175 eÅ$^{-3}$

6-2 selected bond distances

<table>
<thead>
<tr>
<th>Bond</th>
<th>C1-C1'</th>
<th>C1-C2</th>
<th>C1-C19</th>
<th>C2-C6</th>
<th>C2-C3</th>
<th>C6-C5</th>
<th>C3-C4</th>
<th>C4-N1</th>
<th>C5-N1</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(Å)</td>
<td>1.479(13)</td>
<td>1.522(8)</td>
<td>1.532(9)</td>
<td>1.364(9)</td>
<td>1.414(9)</td>
<td>1.379(8)</td>
<td>1.443(7)</td>
<td>1.334(7)</td>
<td>1.331(7)</td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms: i: -x,-y+1,-z

<table>
<thead>
<tr>
<th>Bond</th>
<th>C25-C26</th>
<th>C25-C29</th>
<th>C26-C27</th>
<th>C29-C28</th>
<th>C28-N2</th>
<th>C27-N2</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(Å)</td>
<td>1.382(8)</td>
<td>1.406(8)</td>
<td>1.375(9)</td>
<td>1.388(9)</td>
<td>1.340(9)</td>
<td>1.351(8)</td>
</tr>
</tbody>
</table>

7- Electrochemical data

Redox potential of compounds 2
Electrochemical data for monopyrans 2 in CH2Cl2 with Bu4NPF6 as supporting electrolyte at 0.1 V/s. E vs FeCp2+/FeCp2. (a) irreversible peak. (b) on the reverse cathodic scan.

<table>
<thead>
<tr>
<th>compound</th>
<th>Epa (V) (a)</th>
<th>Epc (V) (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>0.27</td>
<td>-0.79</td>
</tr>
<tr>
<td>1c</td>
<td>0.31</td>
<td>-0.79</td>
</tr>
<tr>
<td>1b</td>
<td>0.30</td>
<td>-0.78</td>
</tr>
</tbody>
</table>

8- Formation of spiropyran 5

Proposed mechanism for the formation of spiropyran 5