

Supporting Information

Coupled molecular motions driven by light or chemical inputs: spiropyran to merocyanine isomerisation followed by pseudorotaxane formation

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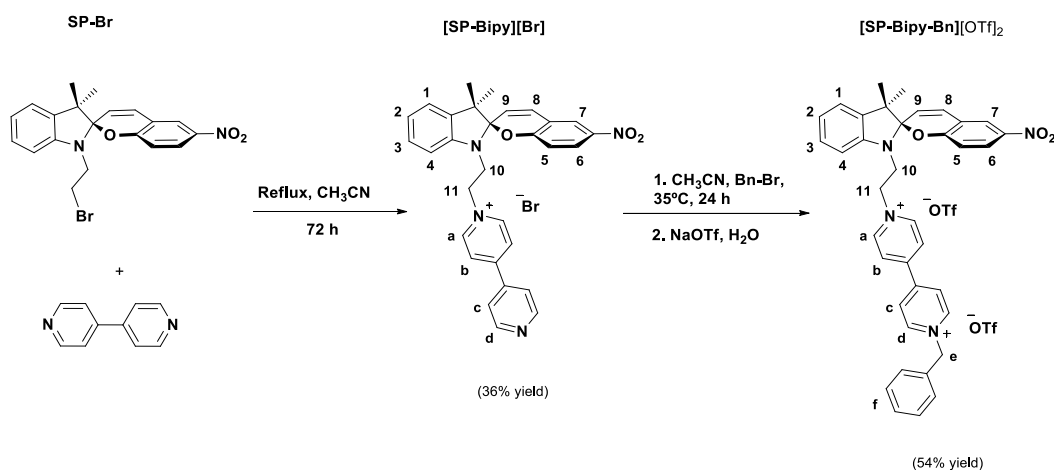
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1. Experimental section

Chemicals were purchased from Aldrich and were used without further treatment. Nuclear Magnetic Resonance spectra (NMR) were recorded on a Jeol 500, Jeol 400, Bruker 300 and Jeol 270. ^1H and ^{13}C NMR chemical shifts were reported in parts per million (ppm) considering Me_4Si as external standard. J values are given in Hz; multiplicity is denoted as follows: s (singlet), d (doublet), dd (doublet of doublets), td (triplet of doublets), br (broad signal). High-resolution mass spectra were recorded on an Agilent G1969A ESI-TOF mass spectrometer. Electronic spectra were recorded on an Agilent Cary 8454 UV-Visible spectroscopy system. UV light irradiation at 254 nm was performed during 1 min using a homemade photoreactor containing 7 UV light lamps (30cm / 8 Watts each).

1.1. Synthesis and characterization of spiropyran-based molecules



Scheme S1: General synthesis of spiropyran-based molecules.

N-(2-Bromoethyl)spirobenzopyran, SP-Br, was obtained as described in literature.¹

N-[2-(1-(4,4'-Bipyridyl))ethyl]spirobenzopyran triflate, [SP-Bipy][OTf]: 1.0 g de **SP-Br** (2.4 mmol) and 4,4'-Bipyridine (1.1 g, 7.2 mmol) were mixed in 6 mL of CH₃CN and heated for 72 hours under reflux. After cooling down to ambient temperature, the mixture was filtered. The resulting solid was washed with CH₃CN (5 mL) and diethyl ether to afford **[SP-Bipy][Br]** (1.08 g, 36%) as a yellow solid. Anionic exchange was performed to obtain the corresponding triflate salt by dissolving the bromide salt in boiling water with 5 equivalents of sodium triflate. The solution was cooled to room temperature and filtered. The solid was washed with cold water and dried under vacuum to obtain **[SP-Bipy][OTf]** (0.17 g, 74%).

δ_{H} (500 MHz; CD₃CN): 8.83 (2H, d, $^3J_{\text{d,c}}$ 6.0, H_d), 8.68 (2H, d, $^3J_{\text{a,b}}$ 7.1, H_a), 8.28 (2H, d, $^3J_{\text{b,a}}$ = 7.1, H_b), 8.01 (1H, d, $^4J_{7,6}$ 2.7, H₇), 7.94 (1H, dd, $^4J_{6,7}$ 2.7, $^3J_{6,5}$ 8.9, H₆), 7.78 (2H, d, $^3J_{\text{c,d}}$ 6.0, H_c), 7.19 (1H, td, $^4J_{3,1}$ 1.1, $^3J_{3,(2,4)}$ 7.8, H₃), 7.15 (1H, br dd, $^3J_{1,2}$ 7.6, H₁), 6.94 (1H, br td, $^3J_{2,(1,3)}$ 7.6, H₂), 6.81 (1H, d, $^3J_{8,9}$ 10.6, H₈), 6.67 (2H, br d, H₄, H₅), 5.08 (1H, d, $^3J_{9,8}$ 10.6, H₉), 4.76 (2H, m, H₁₁), 3.71 (2H, m, H₁₀), 1.18 (3H, s, H_{Me}), 1.04 (3H, s, H_{Me}).

δ_{C} (100 MHz; CD₃CN): 158.7(C_q), 154.5(C_q), 151.3(C_d), 146.0(C_q), 145.6(C_a), 141.5(C_q), 141.0(C_q), 136.5(C_q), 129.3(C₈), 128.0(C₁), 125.9(C_b), 123.0(C₇), 122.3(C₃), 121.9(C_c), 121.2(C₂), 120.0(C₉), 118.7(C_q), 115.7(C₅), 107.3(C₄), 106.2(C_q), 60.2(C₁₁), 52.3(C_q), 45.0(C₁₀), 25.2(C_{Me}), 19.3(C_{Me}).

HR-MS (ESI-TOF): [SP-Bipy]⁺, (C₃₀H₂₇N₄O₃)⁺, *m/z* calculated: 491.2077 amu, *m/z* found: 491.2089 amu, error: 2.4 ppm.

Single crystals were grown by slow evaporation of a saturated solution of **[SP-Bipy][Br]** in methanol. X-ray diffraction data was collected at 173 K on an Enraf-Nonius Kappa diffractometer fitted with a CCD-based detector by using MoKa radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods using SHELXS-97-2² and refined with full-matrix least-squares methods against F^2 data. All non-hydrogen atoms were refined with anisotropic thermal parameters. H atoms were placed in calculated positions and refined anisotropically by using a riding model. Molecular structure drawings were generated by using DIAMOND for Windows.³ Chemical formula: C₃₀H₂₇Br₁O₃N₄, Mw = 571.47, triclinic, *P*-1, *a* = 8.1126(2), *b* = 18.8402(6), *c* = 19.4228(6) Å, α = 88.825(1), β = 88.363(2), γ = 84.224(2), *V* = 2951.90 Å³, *Z* = 4. CCDC 1418311 (See Fig. S7).

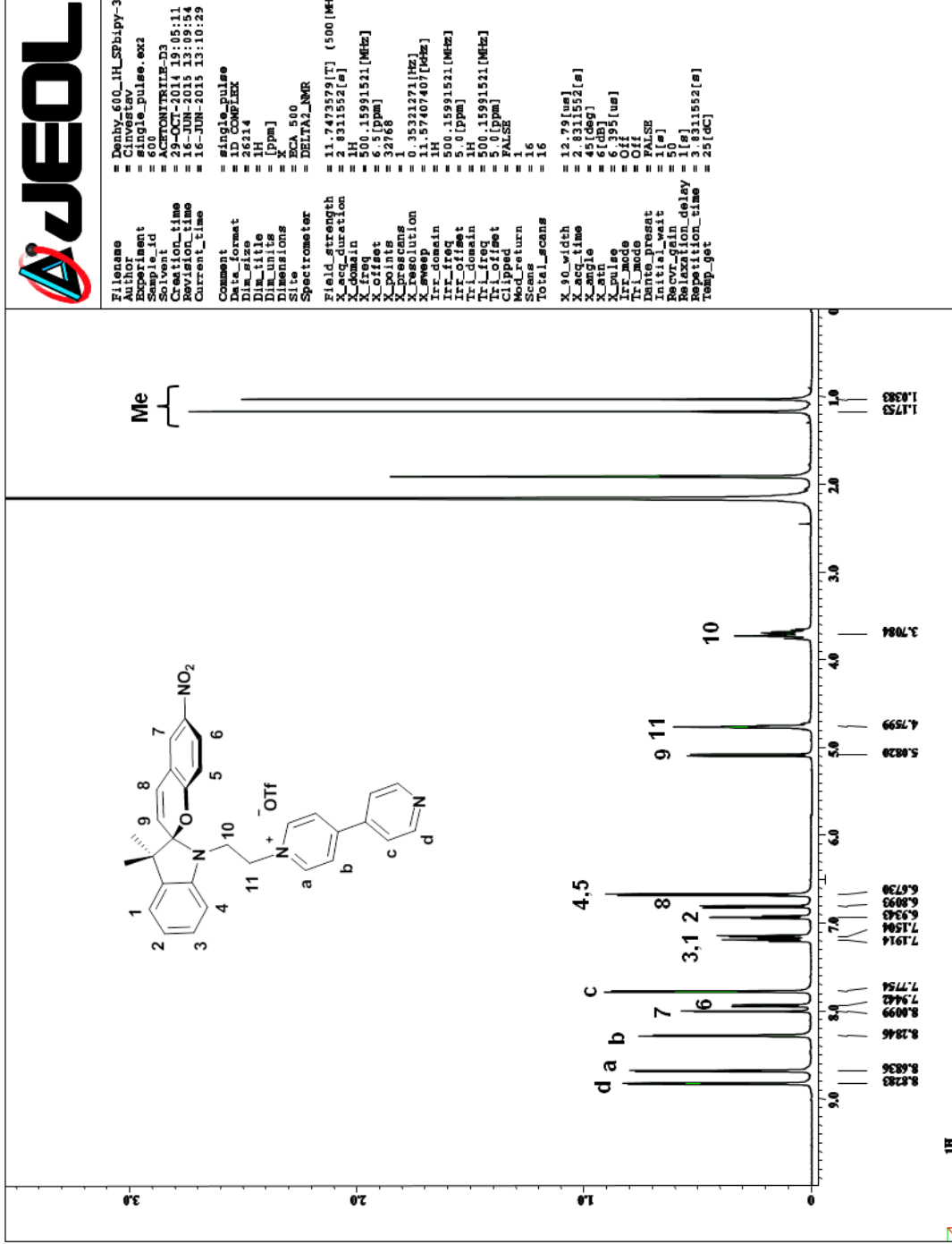


Fig. S1 ^1H NMR spectrum of [SP-Bipy][OTf] (22 mM, CD_3CN , 500 MHz)

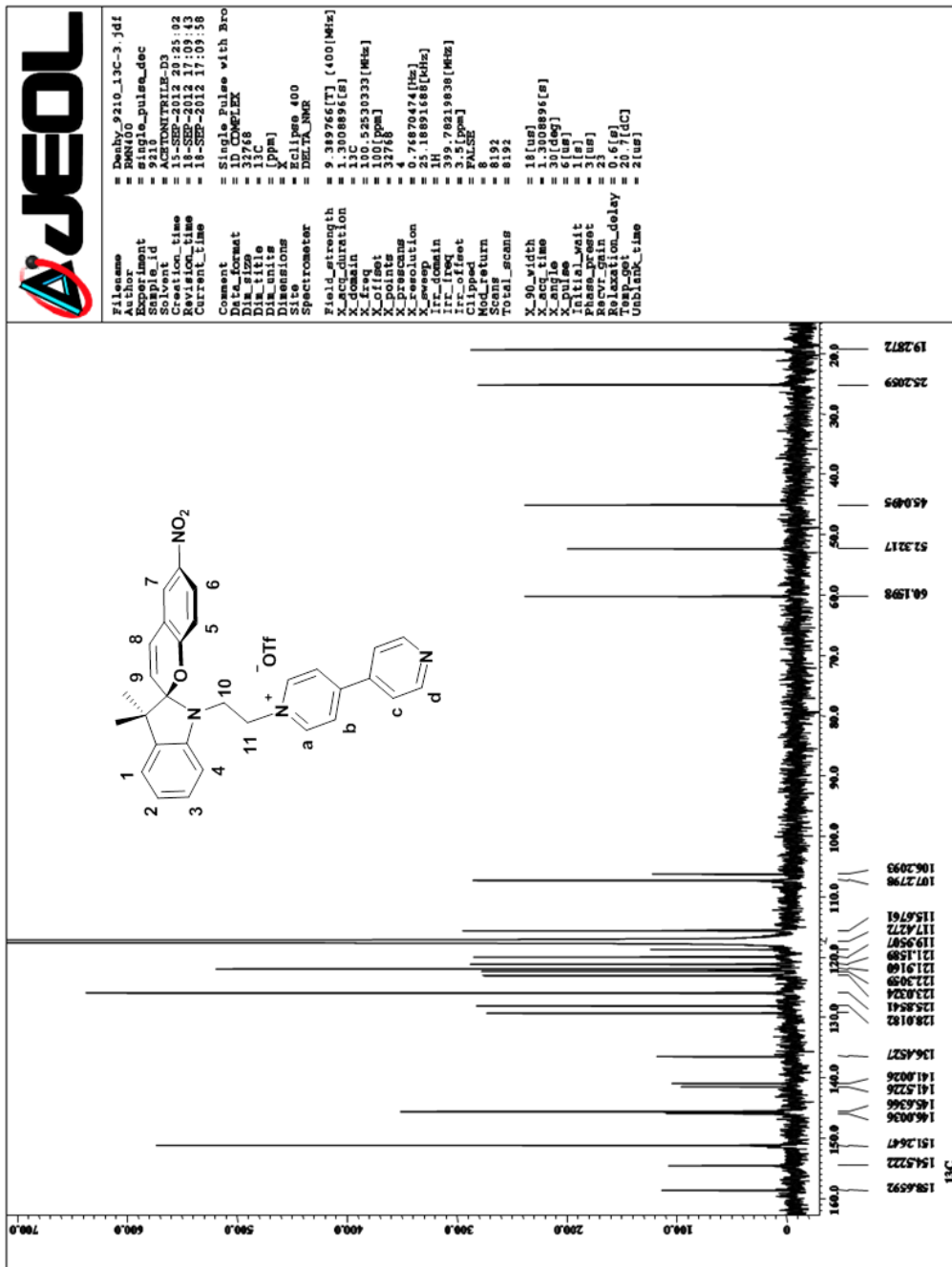


Fig. S2. ^{13}C $\{^1\text{H}\}$ NMR spectrum of [SP-Bipy][OTf] (22 mM, CD_3CN , 100 MHz)

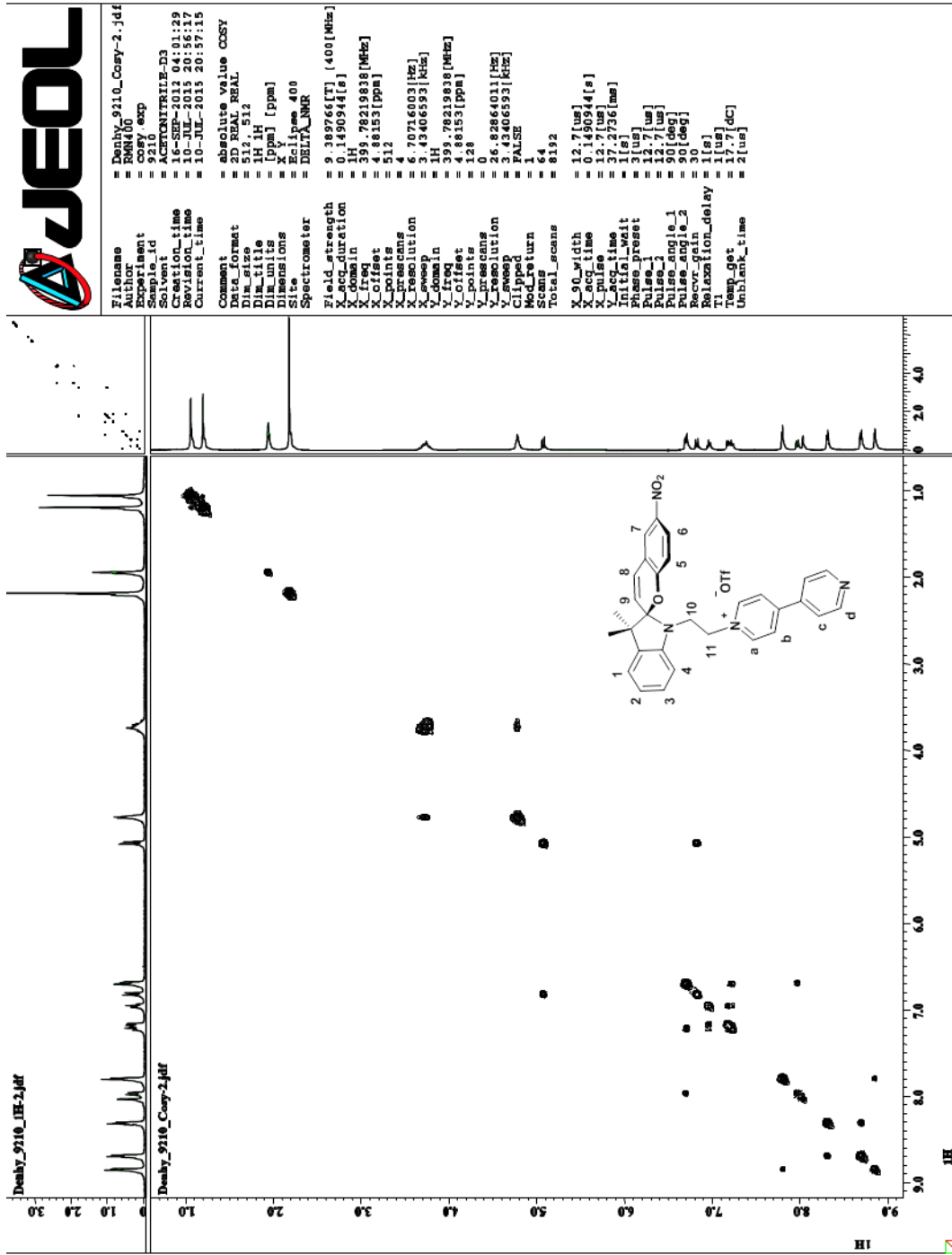


Fig. S3 .2D-COSY NMR spectrum of [SP - Bipy][OTf] (22 mM, CD₃CN, 400 MHz)

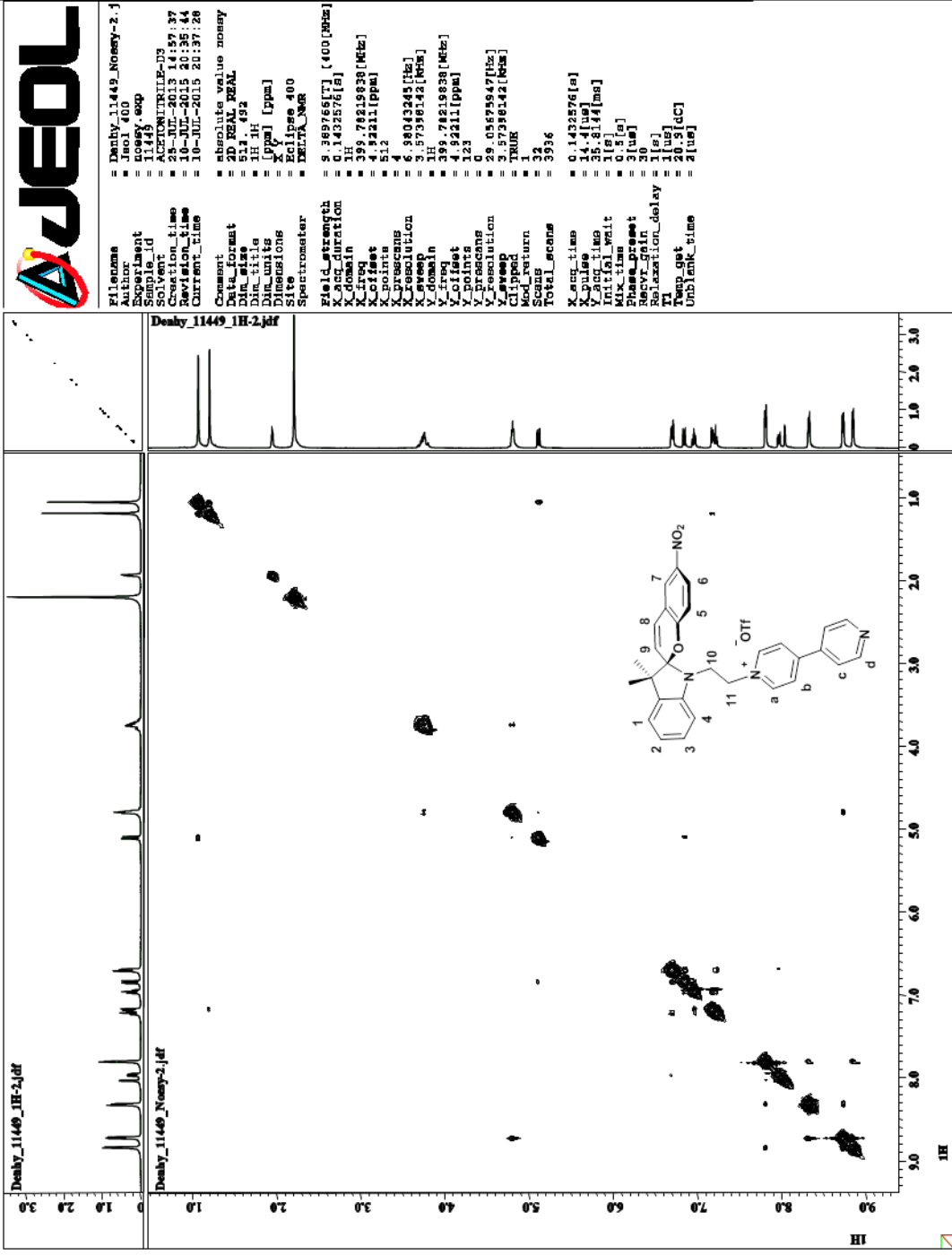


Fig. S4. 2D-NOESY NMR spectrum of [SP-Bipy][OTf] (22 mM, CD₃CN, 400 MHz)

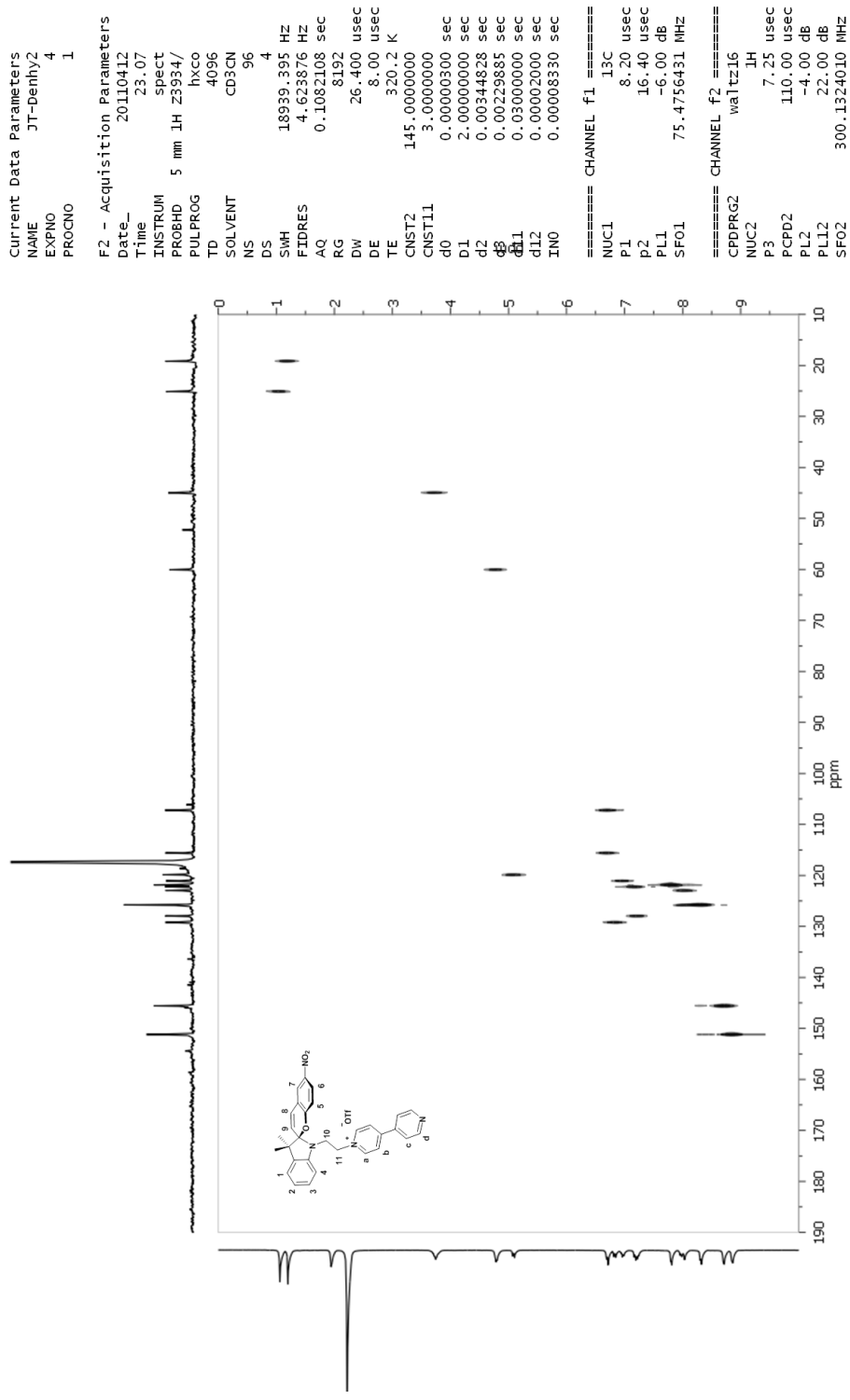


Fig. S5. 2D-HETCOR NMR spectrum of [SP-Bipy][OTf] (22 mM, CD₃CN, 300 MHz)

+TOF MS: 0.209 to 0.226 min from DH-080311-DHM-6-01.wiff Agilent, subtracted (0.953 to 1.Max. 1.4e5 counts).

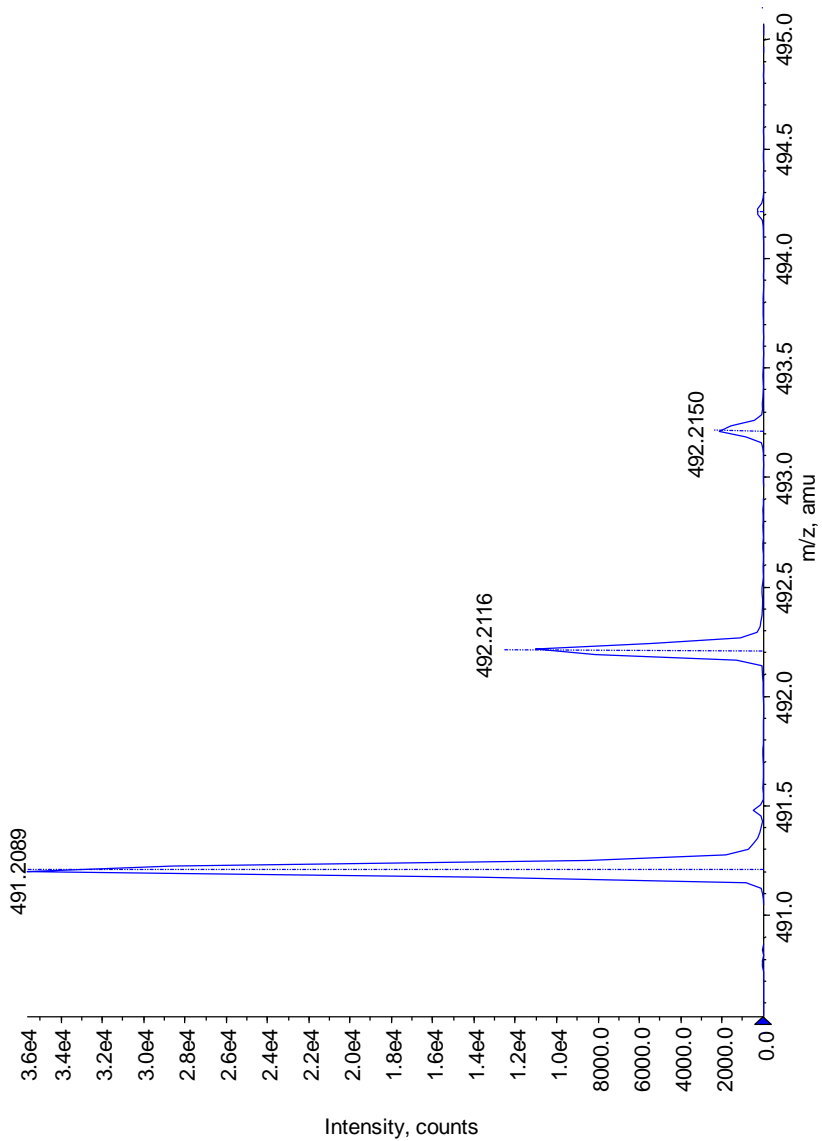


Fig. S6. HR-MS (ESI-TOF) spectrum of **[SP-Bipy]⁺**, **(C₃₀H₂₇N₄O₃)⁺**

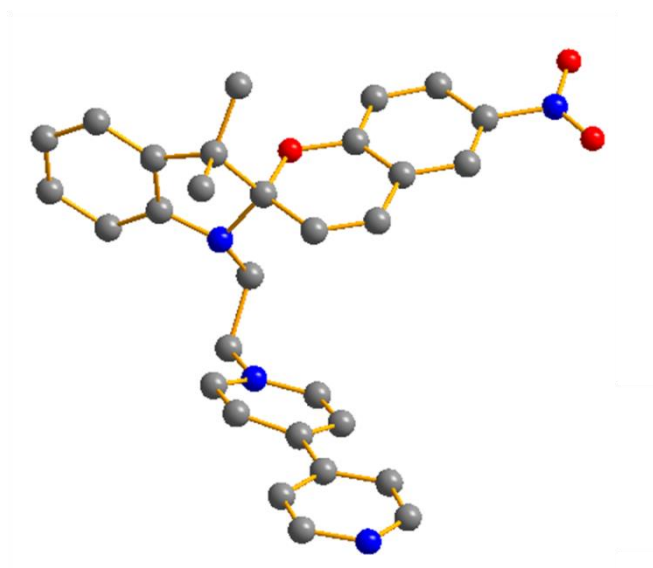


Fig. S7. Ball and stick representation of the X-ray structure of **[SP-Bipy][Br]**. Front view is shown. Hydrogen atoms and anions are omitted for clarity. C = grey; O = red; N = blue.

N-[2-(1-(1'-phenylmethyl)-4,4'-bipyridyl)ethyl] spirobenzopyran ditriflate, [SP-Bipy-Bn][OTf]₂: 0.5 g (0.87 mmol) of **[SP-Bipy][Br]** and 517 μ L of benzyl bromide (4.35 mmol) were combined with 6 mL of CH₃CN and heated to 35°C for 24 hours. Reaction mixture was cooled to room temperature and then diethyl ether was added to precipitate the desired compound. The mixture was cooled with an ice bath and filtered. The solid was washed with diethyl ether and dried under vacuum to yield **[SP-Bipy-Bn][Br]₂** (0.43 g, 67%) as a dark orange solid. Triflate salt was obtained by dissolving the bromide salt in boiling water with 12 equiv. of sodium triflate. The solution was cooled to room temperature and filtered. The solid was washed with cold water and dried under vacuum to obtain **[SP-Bipy-Bn][OTf]₂** as a brown solid (0.27 g, 54%).

δ_{H} (500 MHz, CD₃CN): 9.01 (2H, d, ³J_{d,c} 6.7, H_d), 8.82 (2H, d, ³J_{a,b} 6.7, H_a), 8.43 (2H, d, ³J_{c,d} 6.7, H_c), 8.40 (2H, d, ³J_{b,a} 6.7, H_b), 8.02 (1H, d, ⁴J_{7,6} 2.8, H₇), 7.96 (1H, dd, ⁴J_{6,7} 2.8, ³J_{6,5} 9.2, H₆), 7.50 (5H, m, H_f), 7.20 (1H, td, ⁴J_{3,1} 1.4, ³J_{3,(2,4)} 7.8, H₃), 7.15 (1H, br dd, ³J_{1,2} 7.4, H₁), 6.94 (1H, br td, ³J_{2,(1,3)} 7.4, H₂), 6.82 (1H, d, ³J_{8,9} 10.2, H₈), 6.69 (1H, d, ³J_{4,3} 7.8, H₄), 6.67 (1H, d, ³J_{5,6} 9.2, H₅), 5.83 (2H, s, H_e), 5.05 (1H, d, ³J_{9,8} 10.2, H₉), 4.82 (2H, m, H₁₁), 3.72 (2H, m, H₁₀), 1.18 (3H, s, H_{Me}), 1.03 (3H, s, H_{Me}).

δ_{C} (100 MHz, CD₃CN): 158.7(C_q), 150.3(C_q), 150.1(C_q), 146.4(C_a), 146.0(C_q), 145.7(C_d), 141.6(C_q), 136.5(C_q), 132.8(C_q), 130.2(C_f), 129.7(C_f), 129.5(C_f), 129.4(C₈), 128.0(C₃), 127.6(C_c), 127.2(C_b), 125.9(C₆), 123.1(C₇), 122.3(C₁), 121.2(C₂), 119.9(C₉), 118.7(C_q), 115.7(C₄), 107.4(C₅), 106.2(C_q), 64.8(C_e), 60.8(C₁₁), 52.3(C_q), 45.2(C₁₀), 25.3(C_{Me}), 19.3(C_{Me}).

HR-MS (ESI-TOF): **[SP-Bipy-Bn]²⁺**, (C₃₇H₃₄N₄O₃)²⁺, *m/z* calculated: 291.1309 amu, *m/z* found: 291.1316 amu, error: 2.4 ppm.

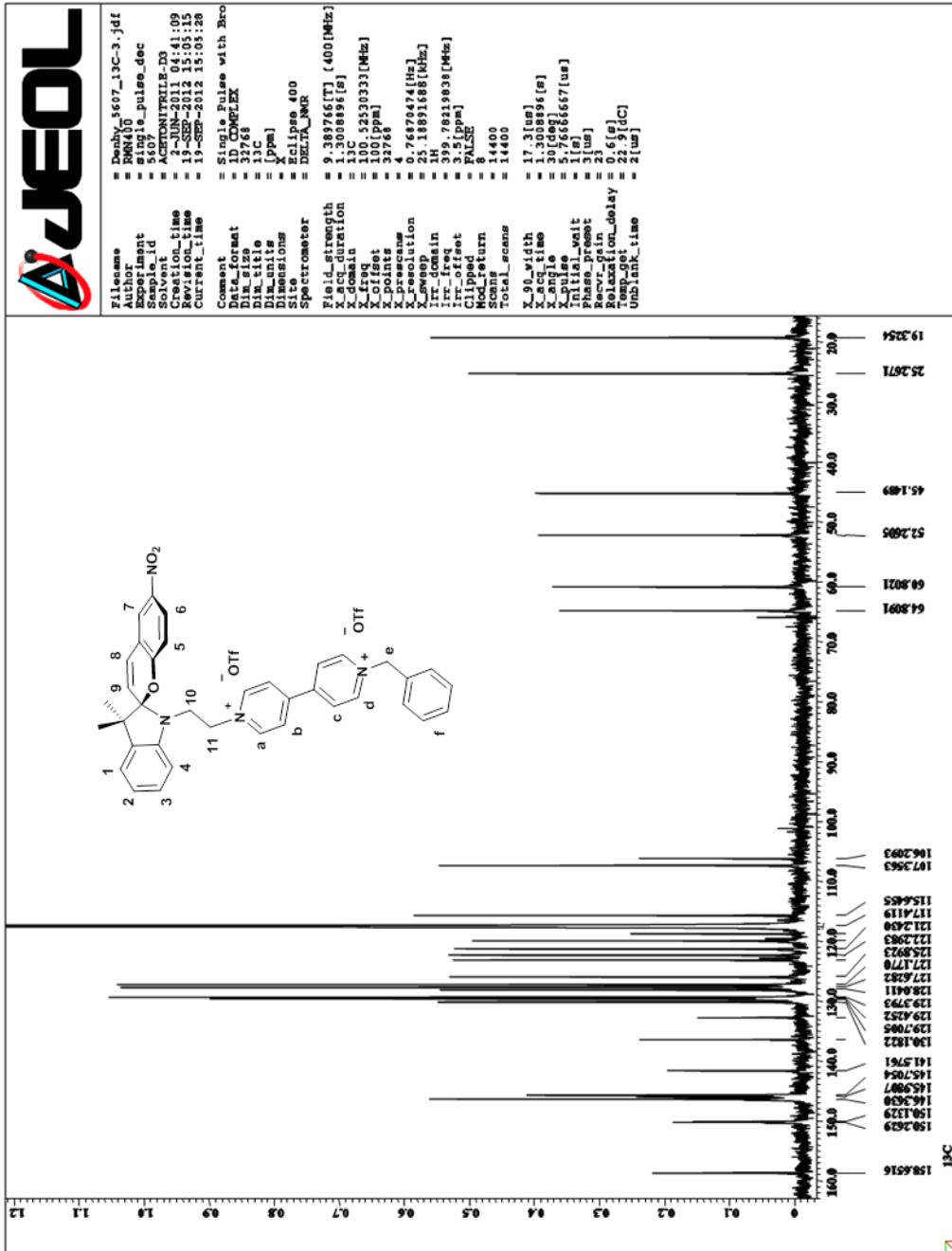


Fig. S9. ^{13}C $\{^1\text{H}\}$ NMR spectrum of [SP-Bipy-Bn][OTf] $_2$ (CD_3CN , 100 MHz)

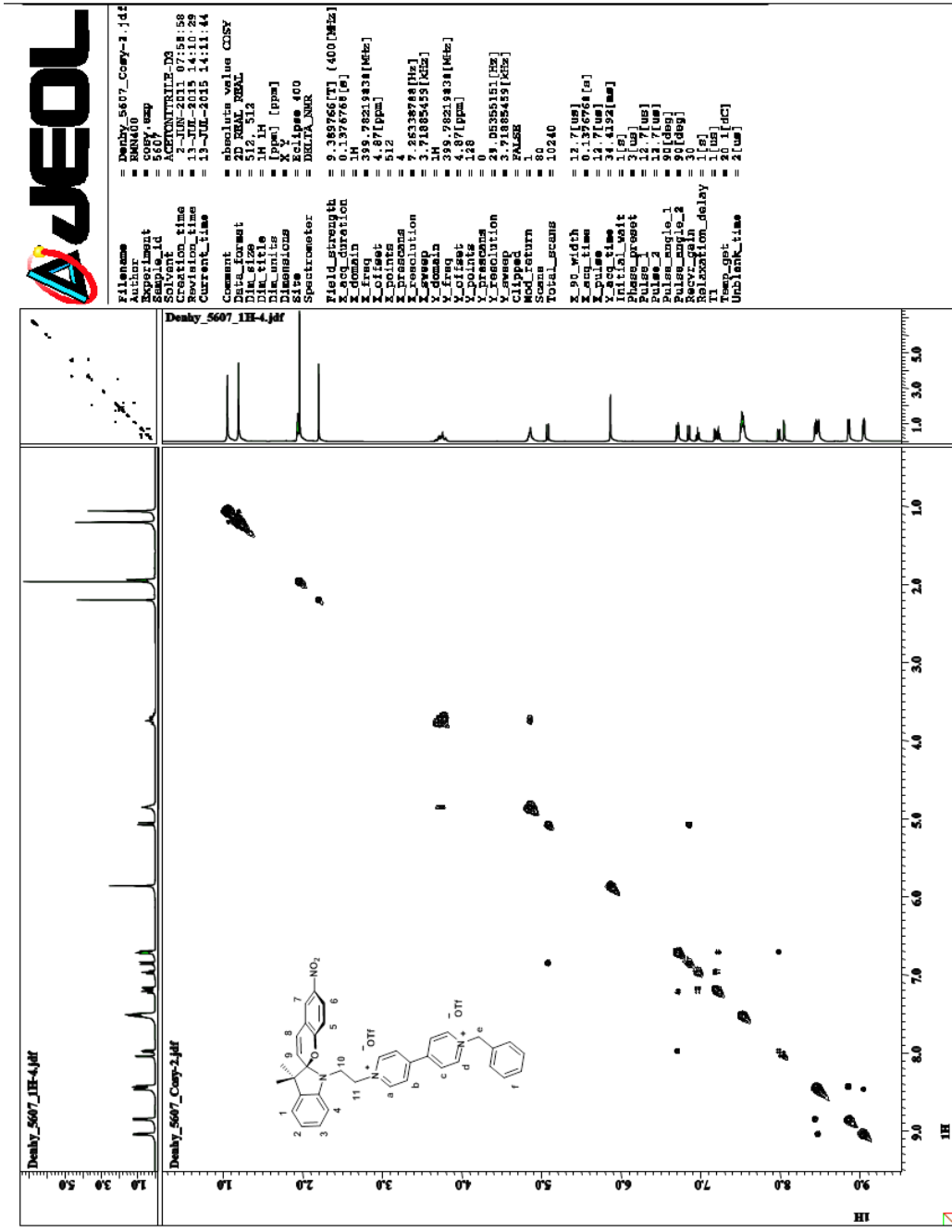


Fig. S10. 2D-COSY NMR spectrum of [SP-Bipy-Bn][OTf]₂ (CD₃CN, 400 MHz)

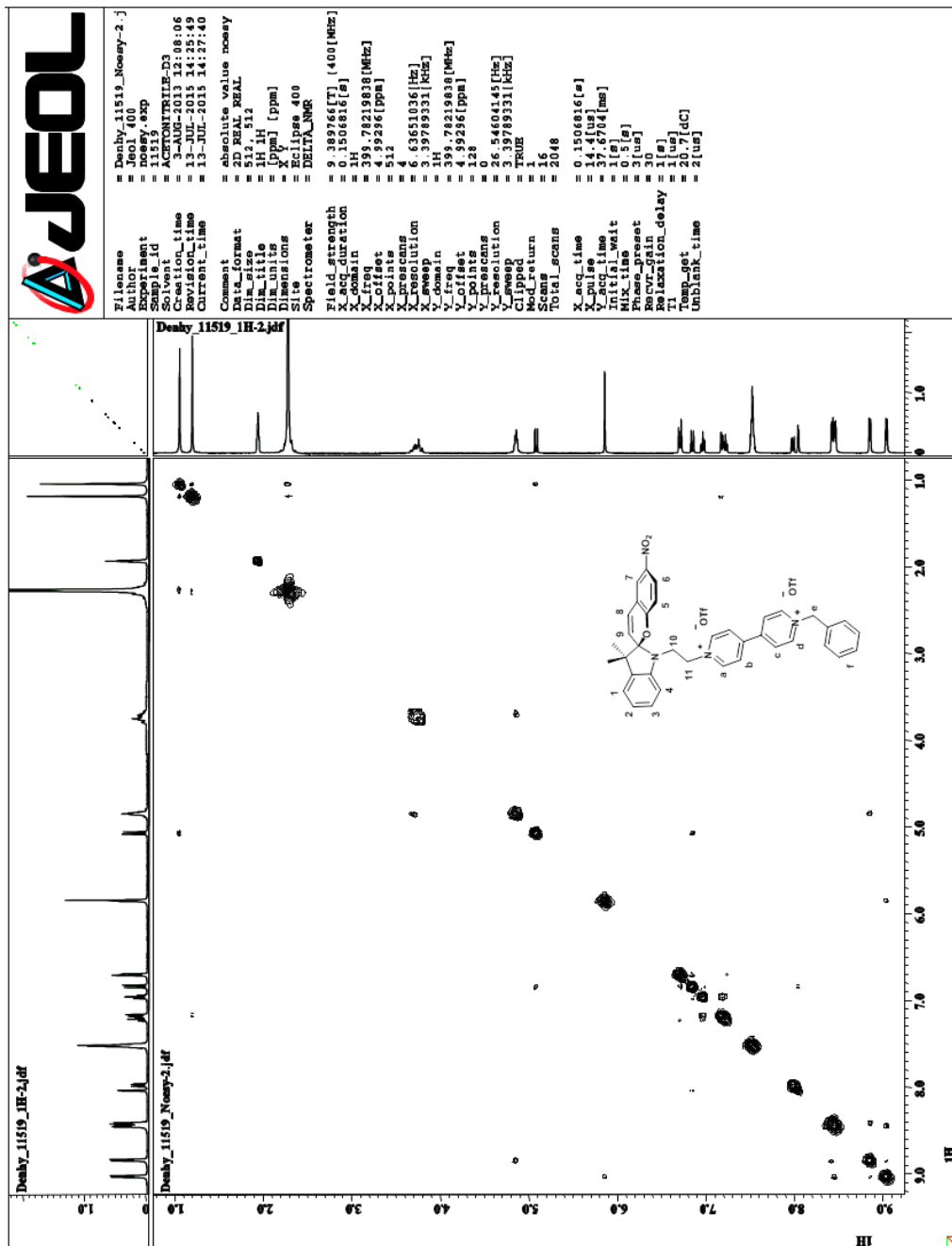


Fig. S11. 2D-NOESY NMR spectrum of [SP-Bipy-Bn][OTf]₂ (CD₃CN, 400 MHz)

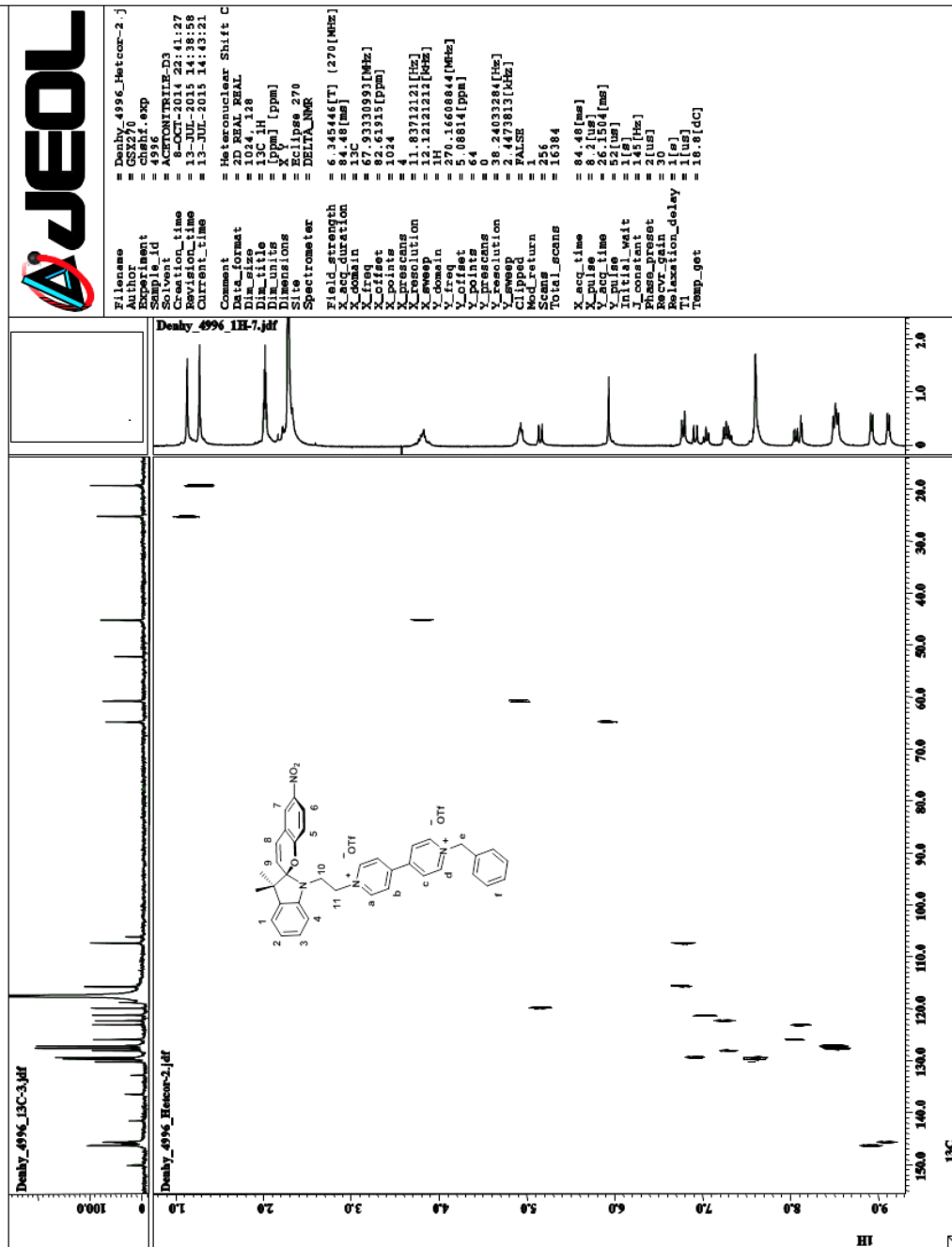


Fig. S12. 2D-HETCOR NMR spectrum of [SP-Bipy-Bn][OTf]₂ (CD₃CN, 270 MHz)

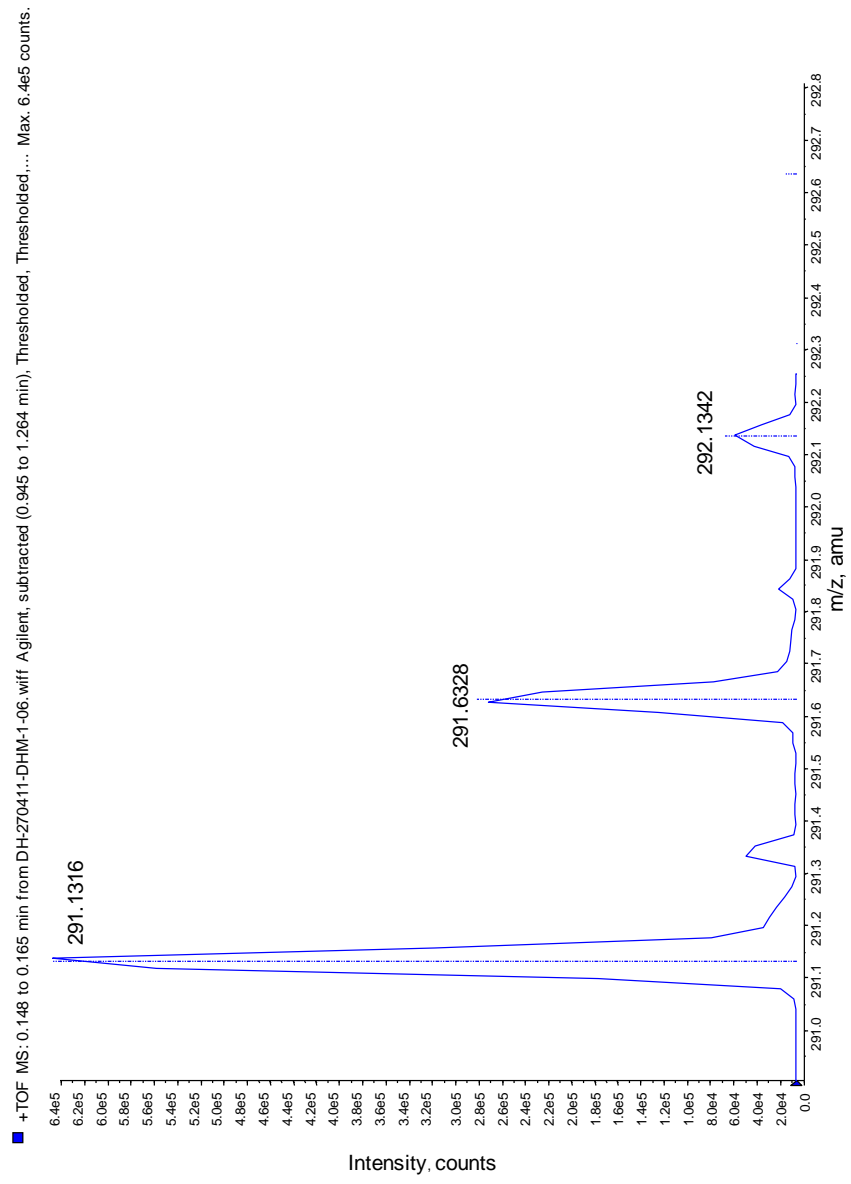


Fig. S13. HR-MS (ESI-TOF) spectrum of $[SP-Bipy-Bn]^{2+}$, $(C_{37}H_{34}N_4O_3)^{2+}$

1.2. Synthesis and characterization of merocyanine-based guests

Spiropyran based axles described previously, were transformed into their protonated merocyanine isomer (**MEH**) *in situ* by adding 3 equiv. of trifluoromethanesulfonate acid (triflic acid, HOTf) to a solution of each axle, in CD₃CN. The transformation is quantitative. Characterization of these guests is described below.

[MEH-Bipy-H][OTf]₃; δ_H (500 MHz, CD₃CN): δ= 9.08 (2H, d, ³J_{a,b} 7.0, H_a), 8.89 (2H, d, ³J_{d,c} 7.0, H_d), 8.63 (1H, d, ⁴J_{7,6} 2.8, H₇), 8.48 (2H, d, ³J_{b,a} 7.0, H_b), 8.36 (1H, d, ³J_{8,9} 16.3, H₈), 8.25 (2H, d, ³J_{c,d} 7.0, H_c), 8.20 (1H, dd, ⁴J_{6,7} 2.8, ³J_{6,5} 9.2, H₆), 7.77 (2H, m, H₁, H₄), 7.68 (1H, br td, ⁴J_{2,4} 1.2, ³J_{2,(1,3)} 7.5, H₂), 7.63 (1H, br td, ⁴J_{3,1} 1.2, ³J_{3,(2,4)} 7.5, H₃), 7.36 (1H, d, ³J_{9,8} 16.3, H₉), 7.18 (1H, d, ³J_{5,6} 9.2, H₅), 5.26 (2H, t, ³J_{11,10} 5.7, H₁₁), 5.19 (2H, t, ³J_{10,11} 5.7, H₁₀), 1.82 (6H, s, H_{Me}).

δ_C (75 MHz, CD₃CN): 185.7(C_q), 163.4(C_q), 151.6(C_q), 150.8(C₈), 146.5(C_a), 143.8(C_q), 142.9(C_d), 141.3(C_q), 140.3(C_q), 130.7(C₃), 130.2(C₆), 129.7(C₂), 128.2(C₇), 128.1(C_b), 126.5(C_c), 123.4(C₄), 122.9(C_q), 120.7(C_q), 118.7(C₅), 114.9(C₁), 113.5(C₉), 58.4(C₁₁), 53.4(C_q), 46.8(C₁₀), 26.0(C_{Me}).

HR-MS (ESI-TOF): [(MEH-Bipy-H)(OTf)]²⁺, (C₃₁H₂₉N₄O₆F₃S)²⁺, *m/z* calculated: 321.0874 amu, *m/z* found: 321.0885 amu, error: 3.4 ppm.

JT-Denhy3
 Brucker 300
 1H (SP-bipy-brn) OTf2 + 3 HOT
 Denhy H.

Current Data Parameters
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 EXPNO 2
 PROCNO 1

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 FIDRES 1.091105 Hz
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 DE 6.00 usec
 TE 314.4 K
 D1 1.00000000 sec
 d11 0.03000000 sec
 TDO 1

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 PL1 -4.00 dB
 SFO1 75.4756731 MHz

==== CHANNEL f2 =====
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 NUC2 1H
 PCPD2 100.00 usec
 PL2 -4.00 dB
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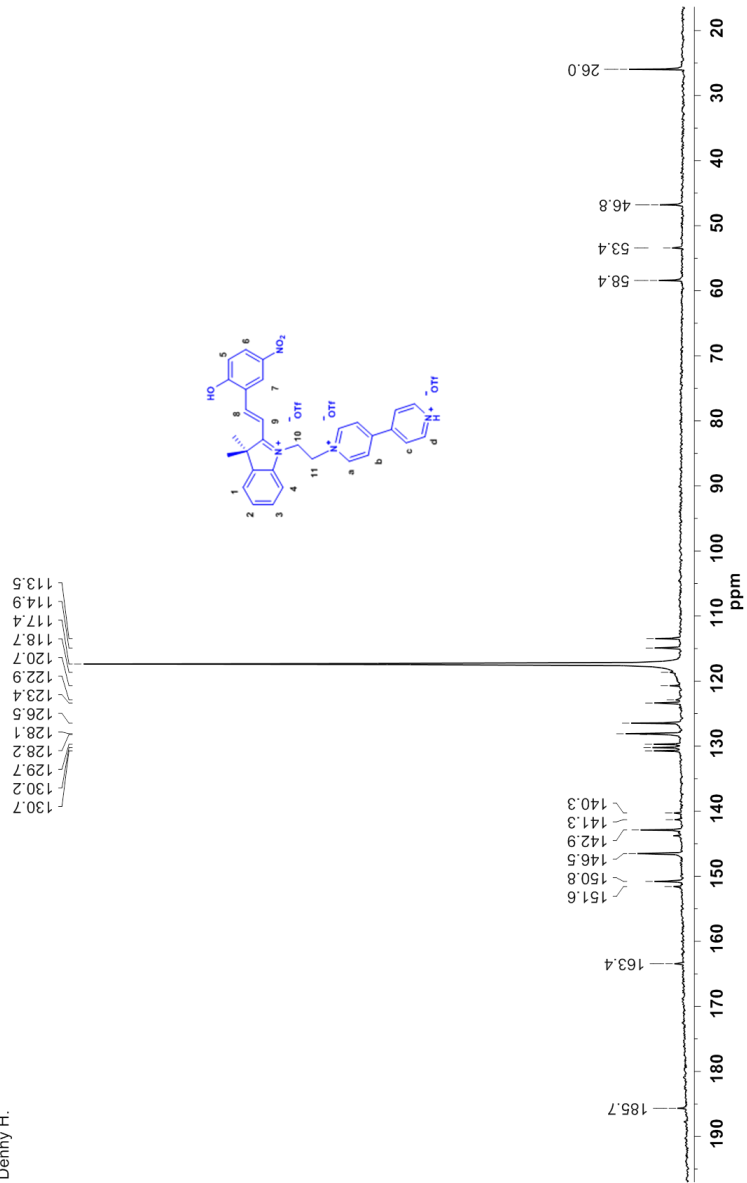


Fig. S15. ¹³C {¹H} NMR spectrum of [MEH-Bipy-H][OTf]₃ (CD₃CN, 75 MHz)

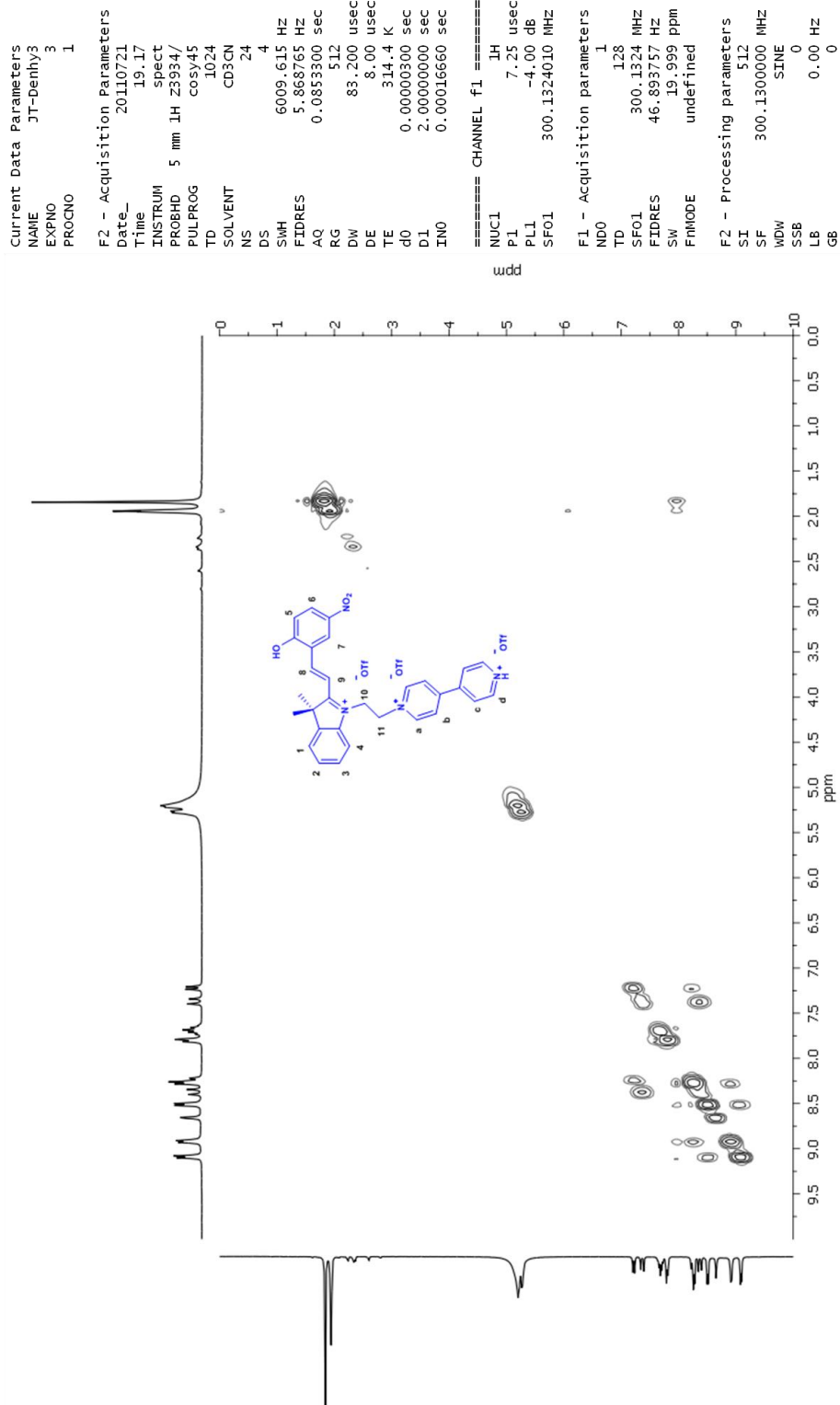


Fig. S16. 2D-COSY NMR spectrum of [MEH-Bipy-H][OTf]₃ (CD₃CN, 300 MHz)

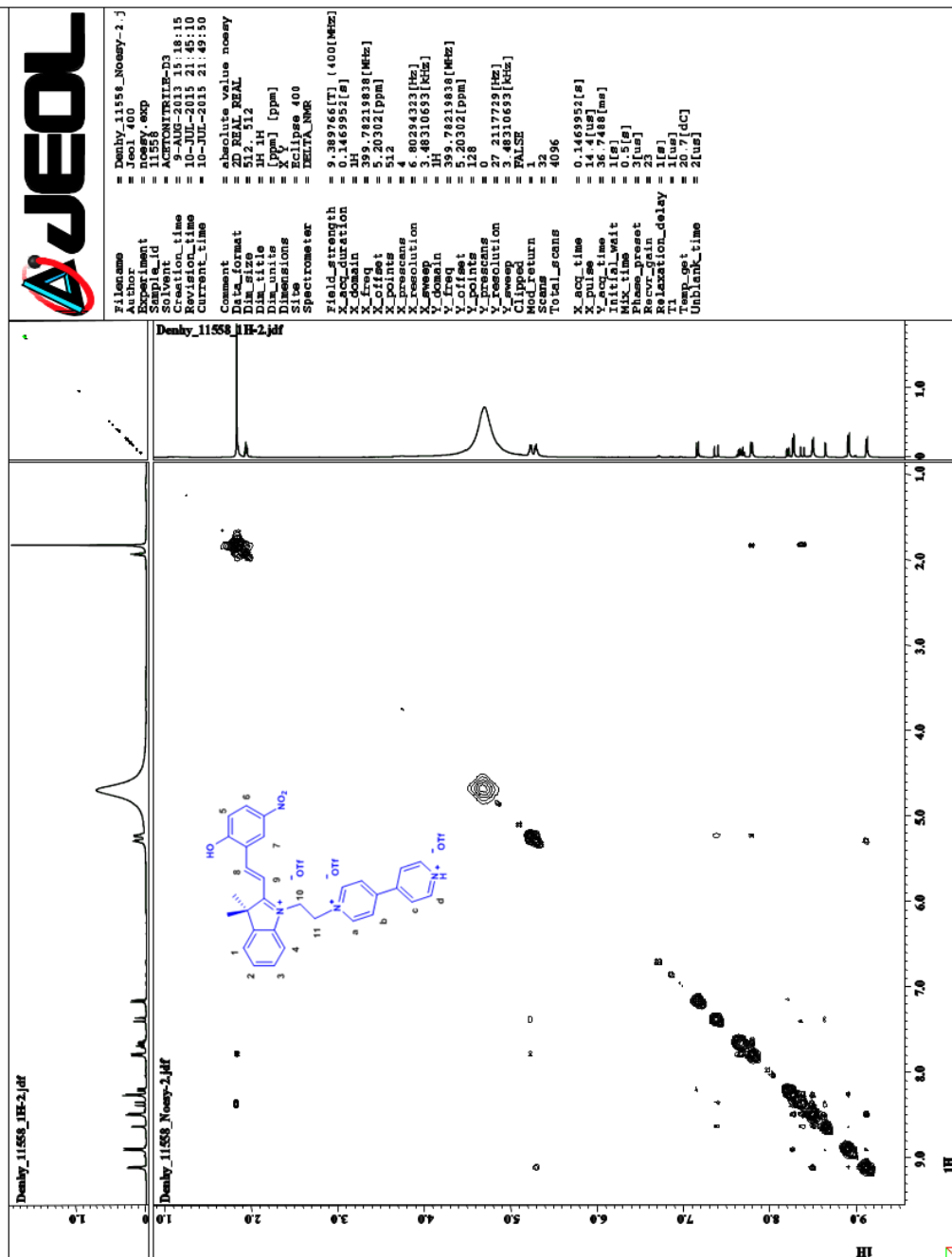


Fig. S17. 2D-NOESY NMR spectrum of [MEH-Bipy-H][OTf]₃ (CD₃CN, 400 MHz)

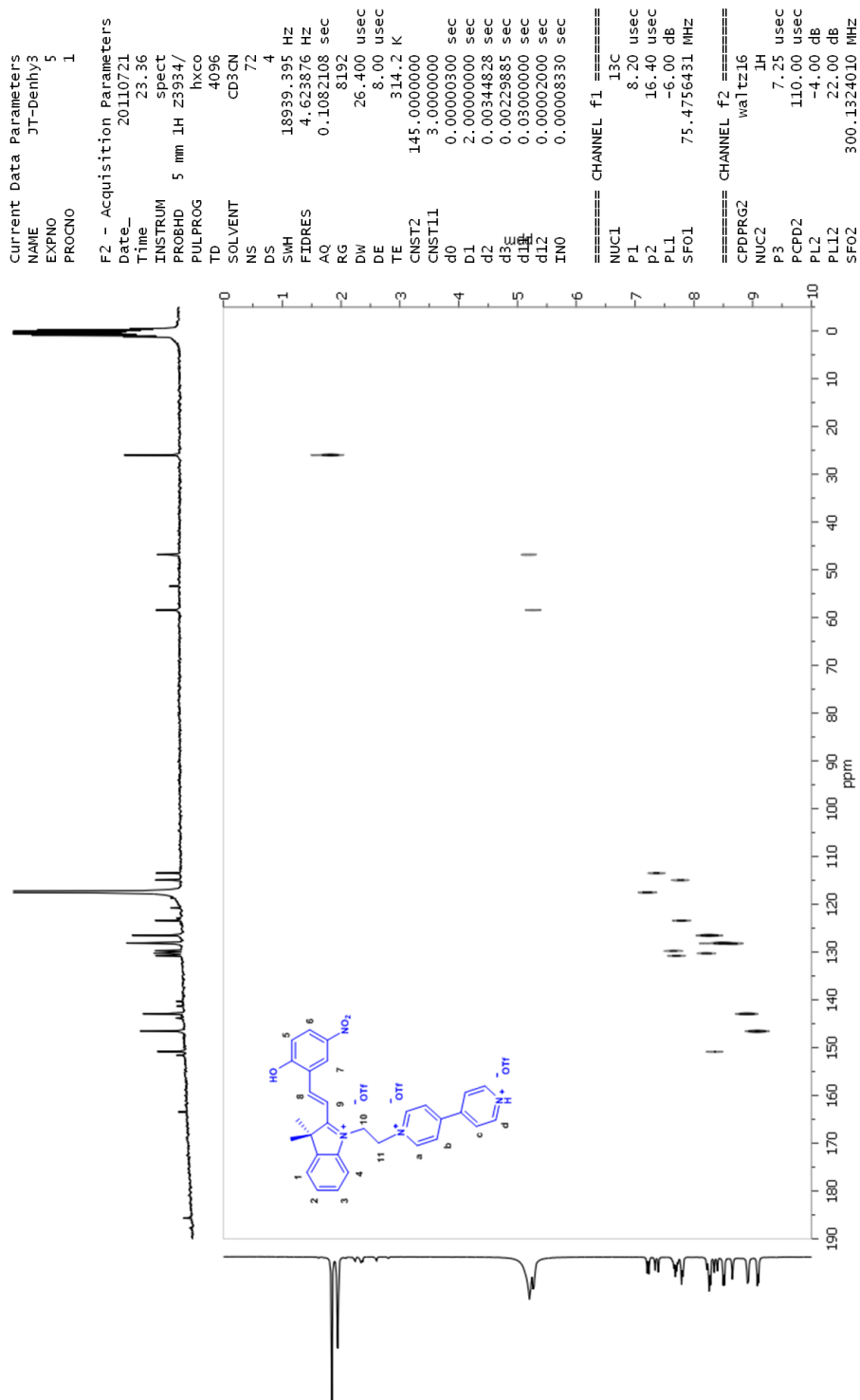


Fig. S18. 2D-HETCOR NMR spectrum of [MEH-Bipy-HJ][OTf]₃ (CD₃CN, 300 MHz)

+TOF MS: 0.126 to 0.162 min from DHM-04-11-14-MEHBIPY-04.wiff Agilent, subtracted (1.1.Max. 6.2e5 counts).

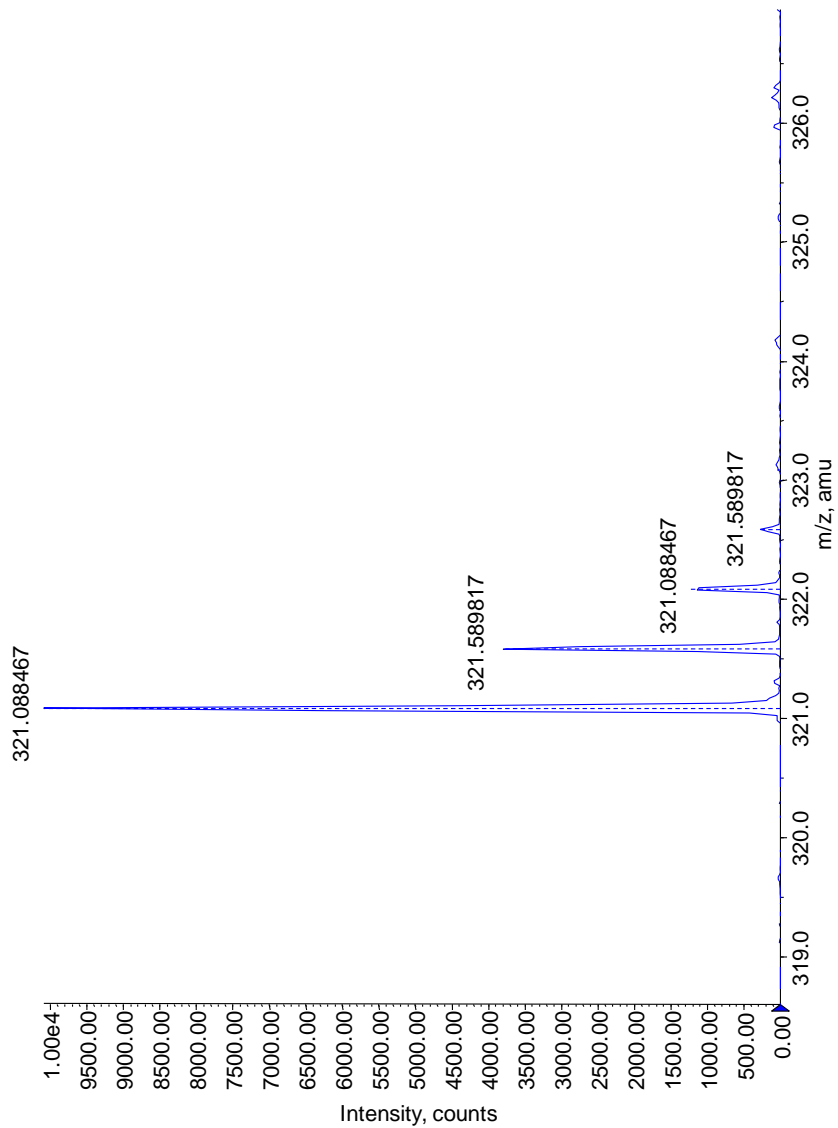


Fig. S19. HR-MS (ESI-TOF) spectrum of [(MEH-Bipy-H)(OTf)]²⁺, (C₃₁H₂₉F₃N₄O₆S)²⁺

[MEH-Bipy-Bn][OTf]₃; δ_{H} (500 MHz, CD₃CN): 9.09 (2H, d, ³J_{a,b} 7.1, H_a), 8.96 (2H, d, ³J_{d,c} 7.1, H_d), 8.63 (1H, d, ⁴J_{7,6} 2.8, H₇), 8.50 (2H, d, ³J_{b,a} 7.1, H_b), 8.37 (1H, d, ³J_{8,9} 16.3, H₈), 8.26 (2H, d, ³J_{c,d} 7.1, H_c), 8.07 (1H, dd, ⁴J_{6,7} 2.8, ³J_{6,5} 9.2, H₆), 7.80 (2H, m, H₁, H₄), 7.71 (1H, br td, ⁴J_{2,4} 1.1, ³J_{2,(1,3)} 7.5, H₂), 7.66 (1H, br td, ⁴J_{3,1} 1.1, ³J_{3,(2,4)} 7.8, H₃), 7.52 (5H, m, H_f), 7.34 (1H, d, ³J_{9,8} 16.3, H₉), 7.19 (1H, d, ³J_{5,6} 9.2, H₅), 5.81 (2H, s, H_e), 5.28 (2H, m, H₁₁), 5.20 (2H, m, H₁₀), 1.84 (6H, s, H_{Me}).

δ_{C} (75 MHz, CD₃CN): 185.7(C_q), 181.0(C_q), 163.4(C_q), 151.1(C_q), 150.7(C₈), 149.3(C_q), 146.5(C_a), 145.6(C_d), 143.8(C_q), 141.3(C_q), 140.3(C_q), 130.7(C₃), 130.2(C_f), 130.1(C₆), 129.7(C₂), 129.6(C_f), 129.3(C_f), 128.1(C₇), 128.0(C_b), 127.3(C_c), 123.4(C₄), 120.7(C_q), 118.4(C₅), 114.9(C₁), 113.4(C₉), 64.8(C_e), 58.5(C₁₁), 53.5(C_q), 46.9(C₁₀), 26.0(C_{Me}).

HR-MS (ESI-TOF): [(MEH-Bipy-Bn)(OTf)₂]⁺, (C₃₉H₃₅N₄O₉F₆S₂)⁺, *m/z* calculated: 881.1744 amu, *m/z* found: 881.1739 amu, error: 0.6 ppm.

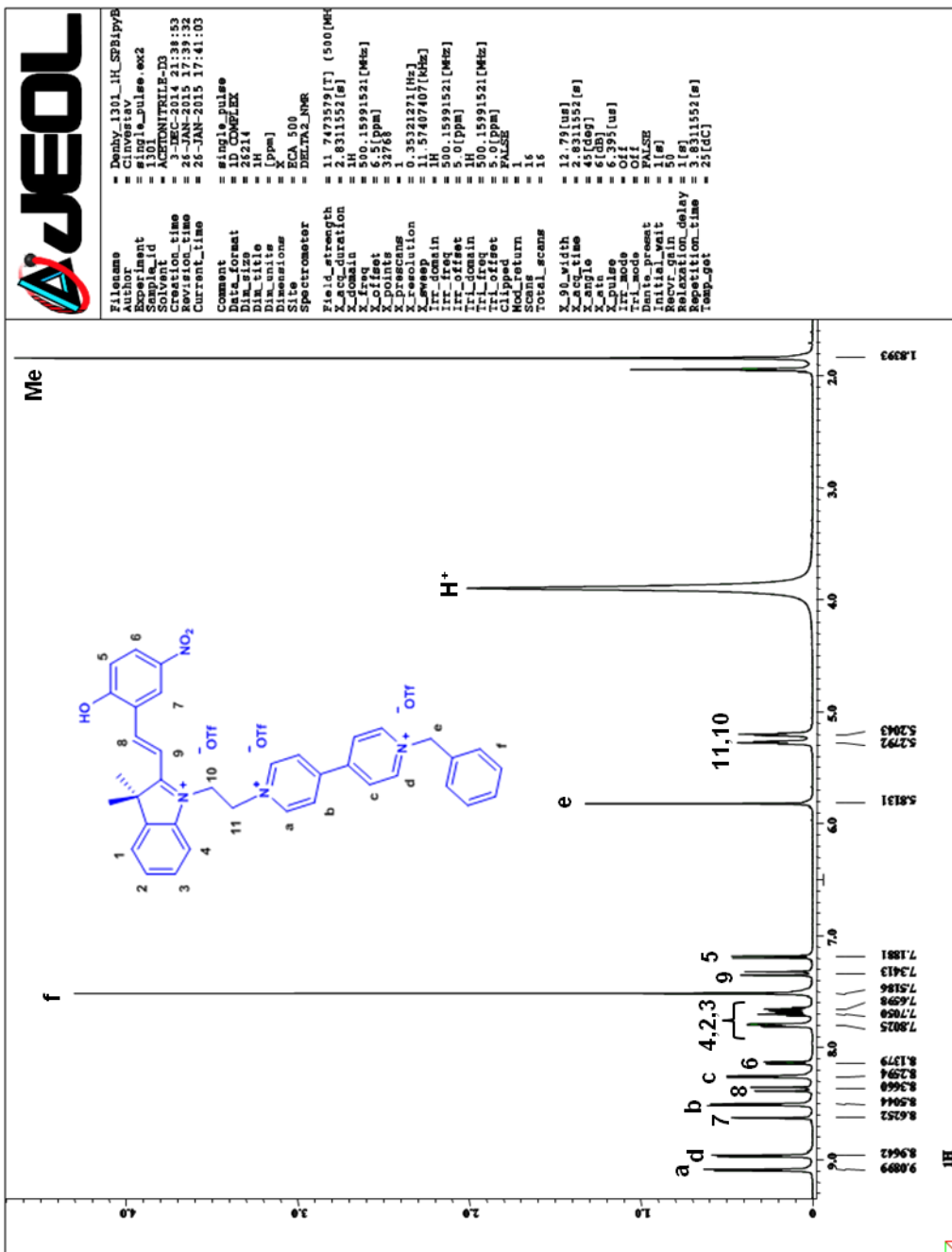


Fig. S20. ^1H NMR spectrum of $[\text{MEH-Bipy-Bn}][\text{OTf}]_3$ (CD_3CN , 500 MHz)

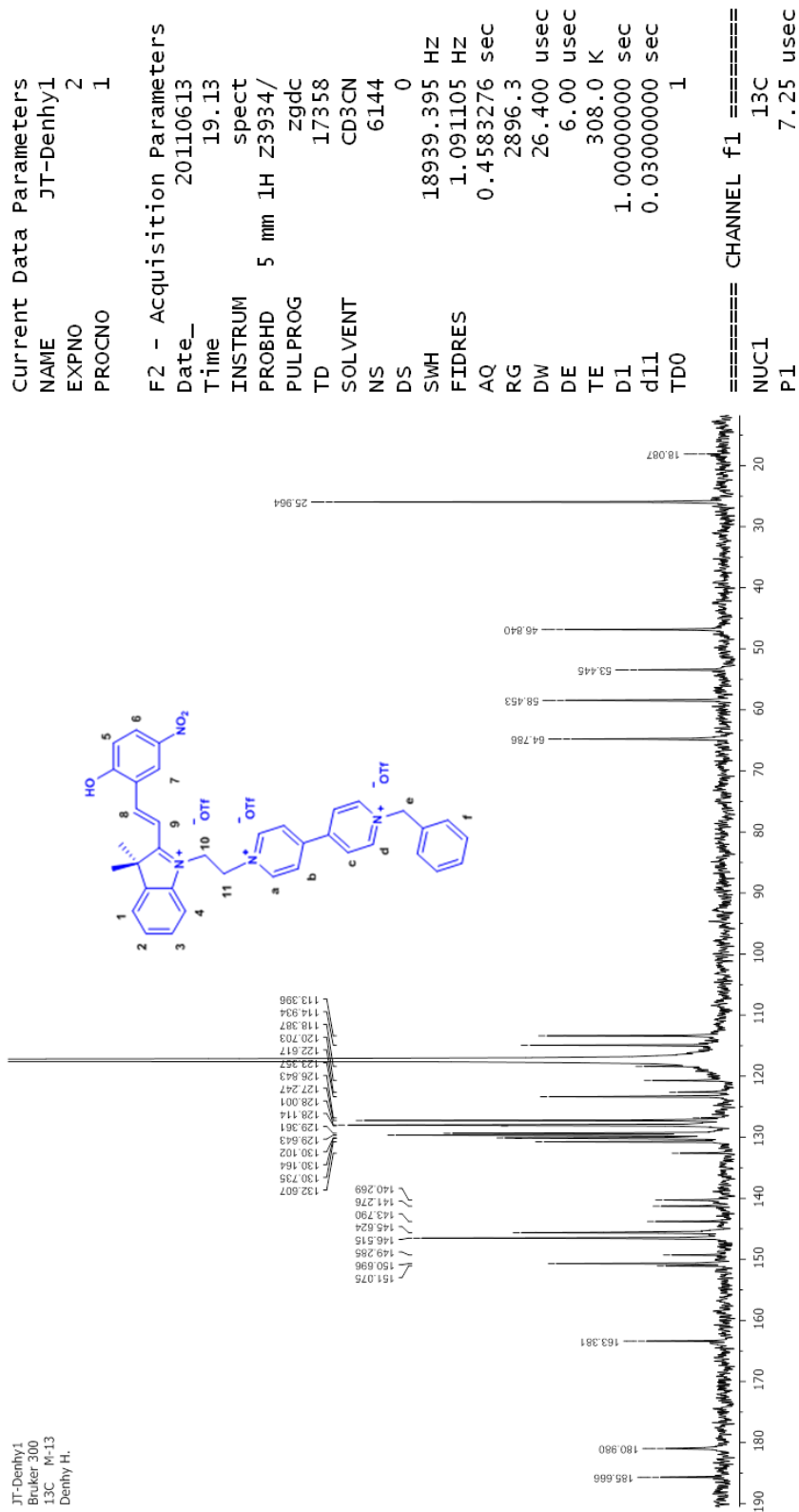


Fig. S21. ^{13}C $\{^1\text{H}\}$ NMR spectrum of $[\text{MEH-Bipy-Bn}]\text{OTf}_3$ (CD_3CN , 75 MHz)

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DE       8.00 usec
TE       307.9 K
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d1       2.00000000 sec
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F1 - Acquisition parameters
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SW       19.999 ppm
F1MODE   undefined

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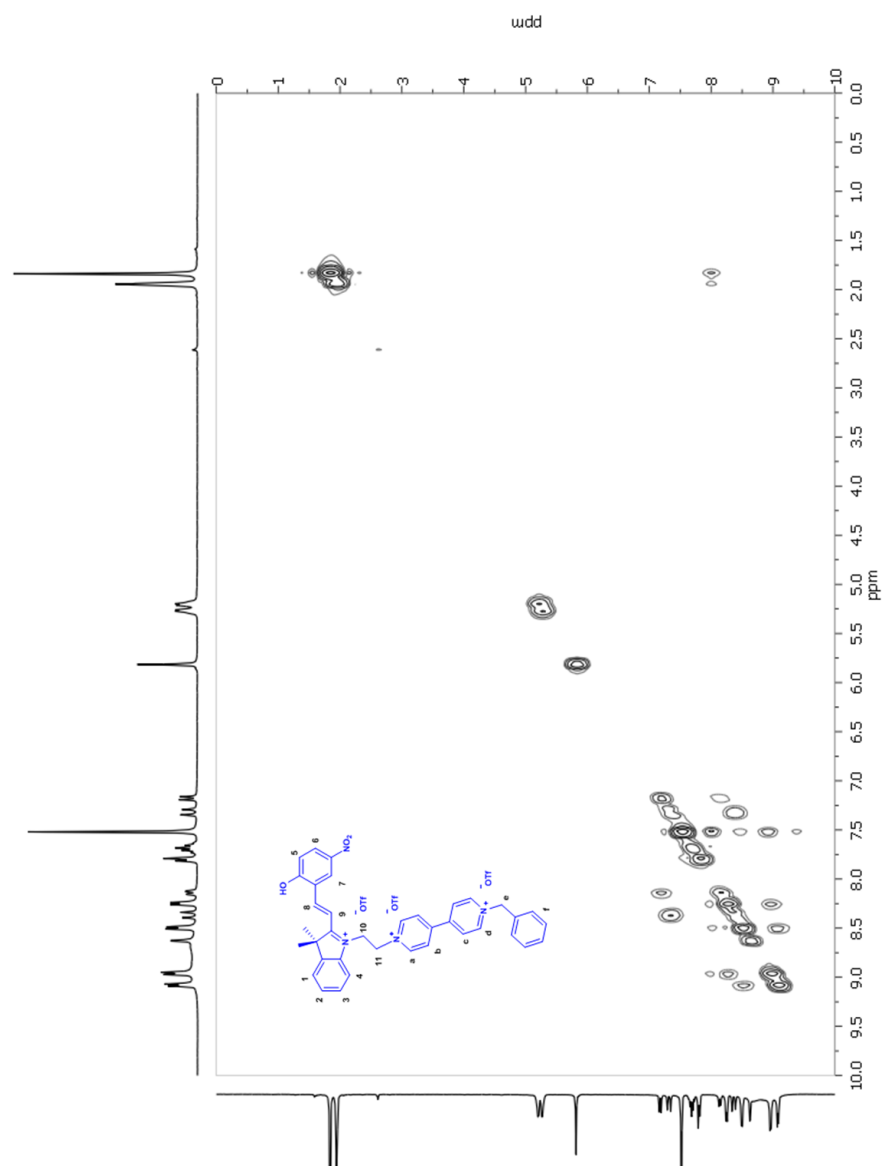


Fig. S22. 2D-COSY NMR spectrum of [MEH-Bipy-Bn][OTf]₃ (CD₃CN, 300 MHz)

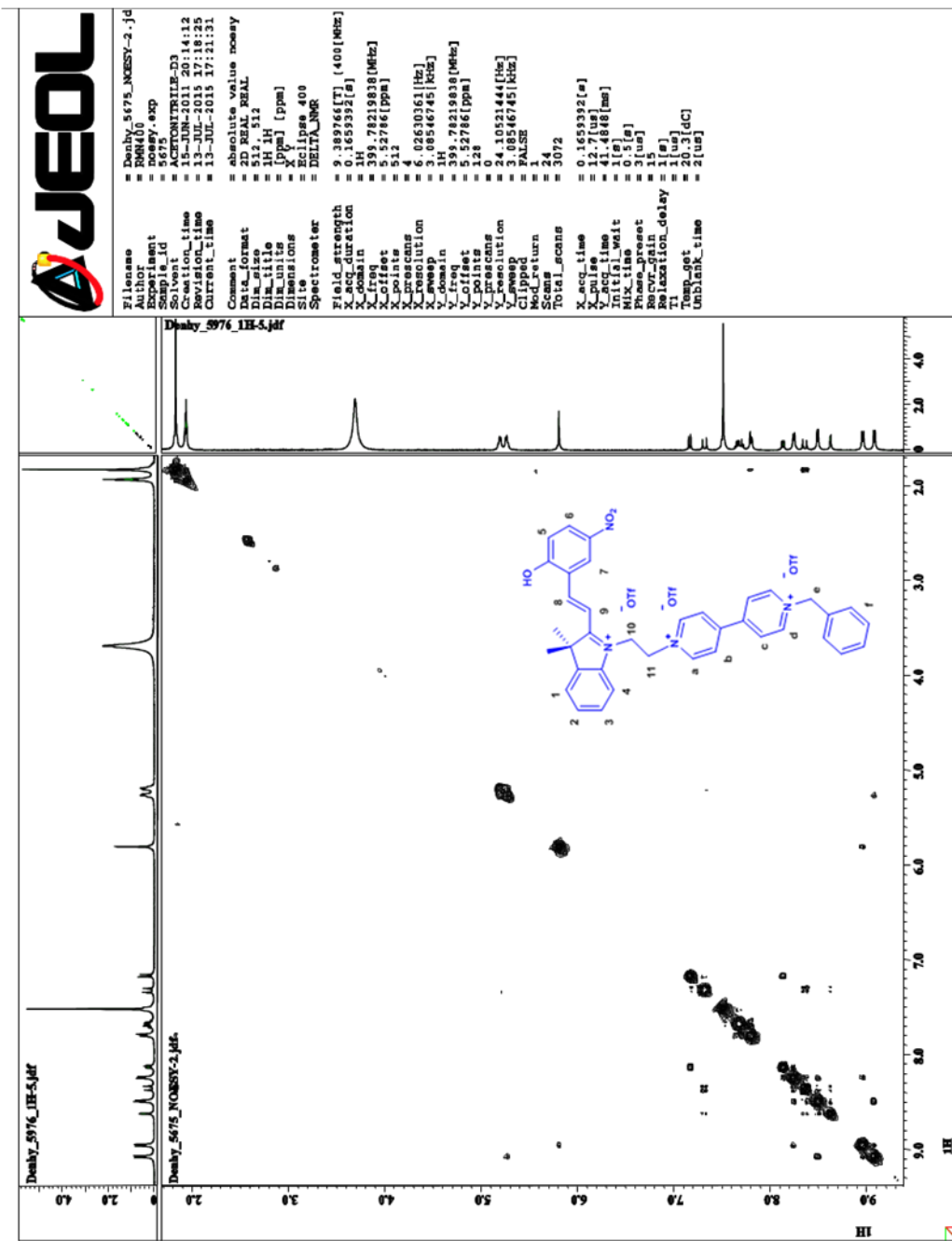


Fig. S23. 2D-NOESY NMR spectrum of [MEH-Bipy-Bn][OTf]₃ (CD₃CN, 400 MHz)

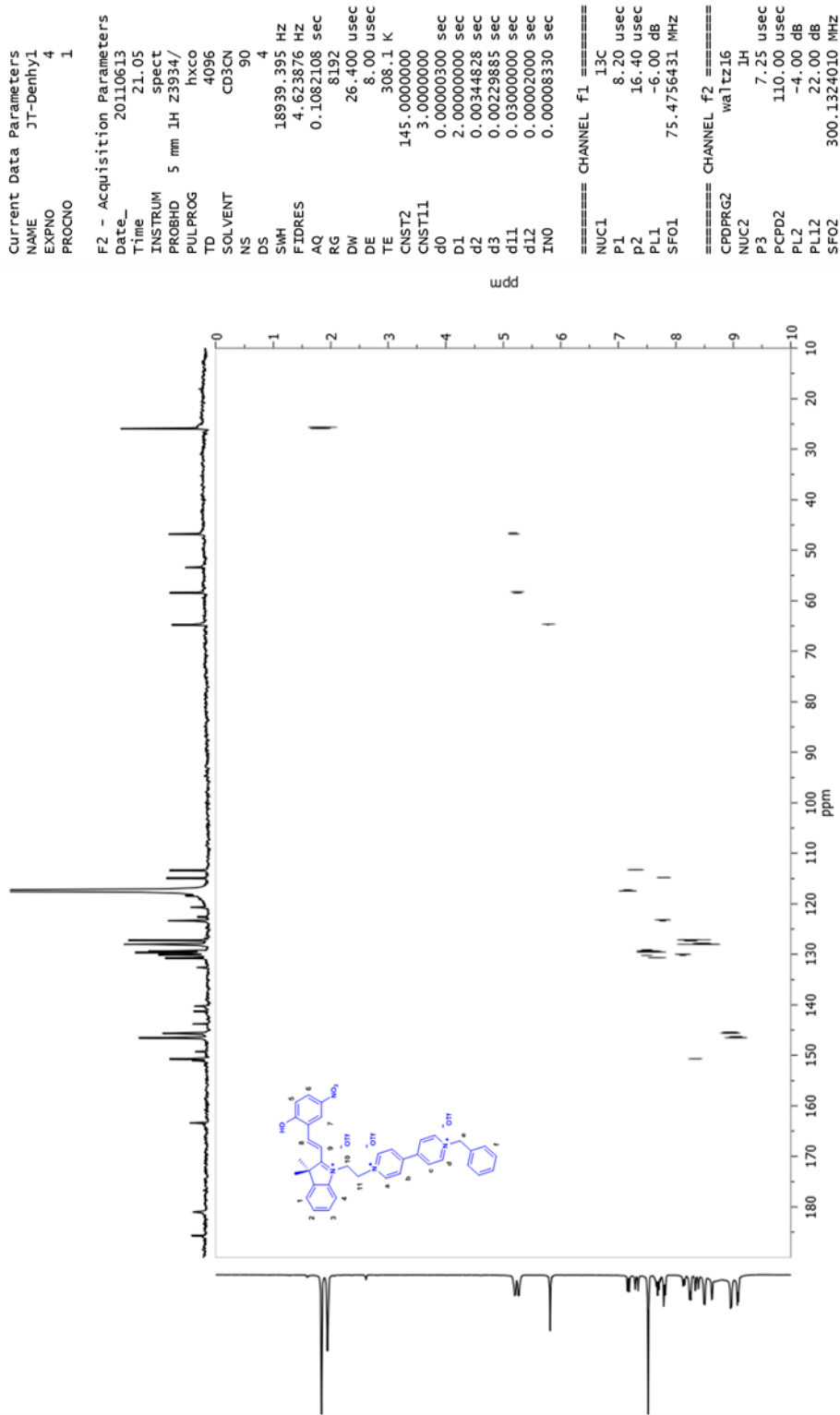


Fig. S24. 2D-HETCOR NMR spectrum of [MEH-Bipy-Bn][OTf]₃ (CD₃CN, 300 MHz)

+TOF MS: 0.112 to 0.129 min from DH-151014-MEHbn-01.wiff Agilent, subtracted (1.104 to .Max. 2.0e5 counts.

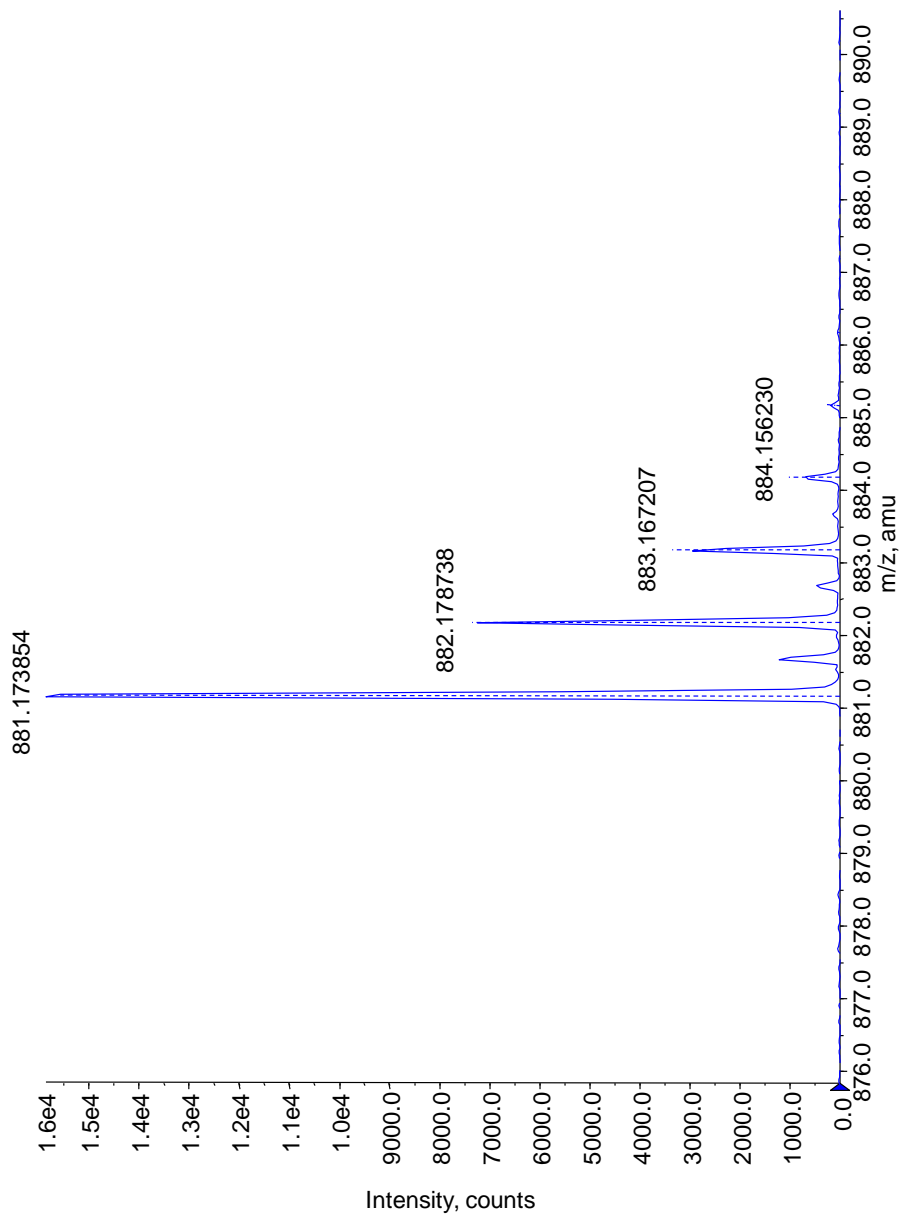


Fig. S25. HR-MS (ESI-TOF) spectrum of [(MEH-Bipy-Bn)(OTf)₂]⁺, (C₃₉H₃₅F₆N₄O₉S₂)⁺

2. Association study between spiropyran/merocyanine-based molecules and DB24C8

2.1. General procedure for estimation of association constants, K_a , for slow and fast chemical exchange

Association constants were determined by analysis of ^1H NMR spectra (CD_3CN , 25 °C, 500 MHz).

A 22 mM solution of **[SP-Bipy][OTf]** was prepared, then increasing amounts of **DB24C8** were added in solid to avoid solvent effects (see Fig. S26 and S27). The solid was weighed by using a Mettler Toledo XP26 Microbalance (0.001 mg of readability).

Merocyanine-based axes, **[MEH-Bipy-H][OTf]₃** and **[MEH-Bipy-Bn][OTf]₃**, were obtained *in situ* by adding 3 μL of triflic acid (0.033 mmol) to a solution 22 mM of the corresponding spiropyran-based compound. After maintaining acidic solution in the dark over 12 hours for completion of the isomerization process, **DB24C8** was added in solid.

Merocyanine axle, **[MEH-Bipy-H][BF₄]₃** was obtained by anion exchange between **[SP-Bipy-Bn][Br]₂** and sodium tetrafluoroborate in water and addition of an aqueous solution of tetrafluoroboric. After maintaining this solution in the dark over 12 hours for completion of the isomerization process, **DB24C8** was added in solid.

Association constant of the complex with fast chemical exchange on the NMR time scale, was estimated by titrating a solution of **[MEH-Bipy-H][OTf]₃** (22mM) with increasing amounts of **DB24C8** until saturation was reached. Changes in chemical shifts of H_{11} and H_{10} resonances were fitted using the software WinEQNMR2.⁴ (See Fig. S28 and S29).

For *pseudorotaxane* with slow chemical exchange on the NMR time scale, a 22 mM solution of **[MEH-Bipy-Bn][OTf]₃** or **[MEH-Bipy-Bn][BF₄]₃** with 3 equivalents of **DB24C8** (0.033 mmol, 15 mg) was prepared. The concentration at equilibrium of the species in solution was determined using the initial thread and macrocycle concentrations, besides the integration of H_{Ar} , H_7 , H_8 or H_{Me} signals of free and complexed species. For guest **[MEH-Bipy-Bn][OTf]₃** the association constant was determined as $K_a = 11 (\pm 2) \text{ M}^{-1}$ and for guest **[MEH-Bipy-Bn][BF₄]₃**, $K_a = 15 (\pm 2) \text{ M}^{-1}$.

2.2. ^1H NMR titration experiment between $[\text{SP-Bipy}][\text{OTf}]$ and DB24C8 in CD_3CN

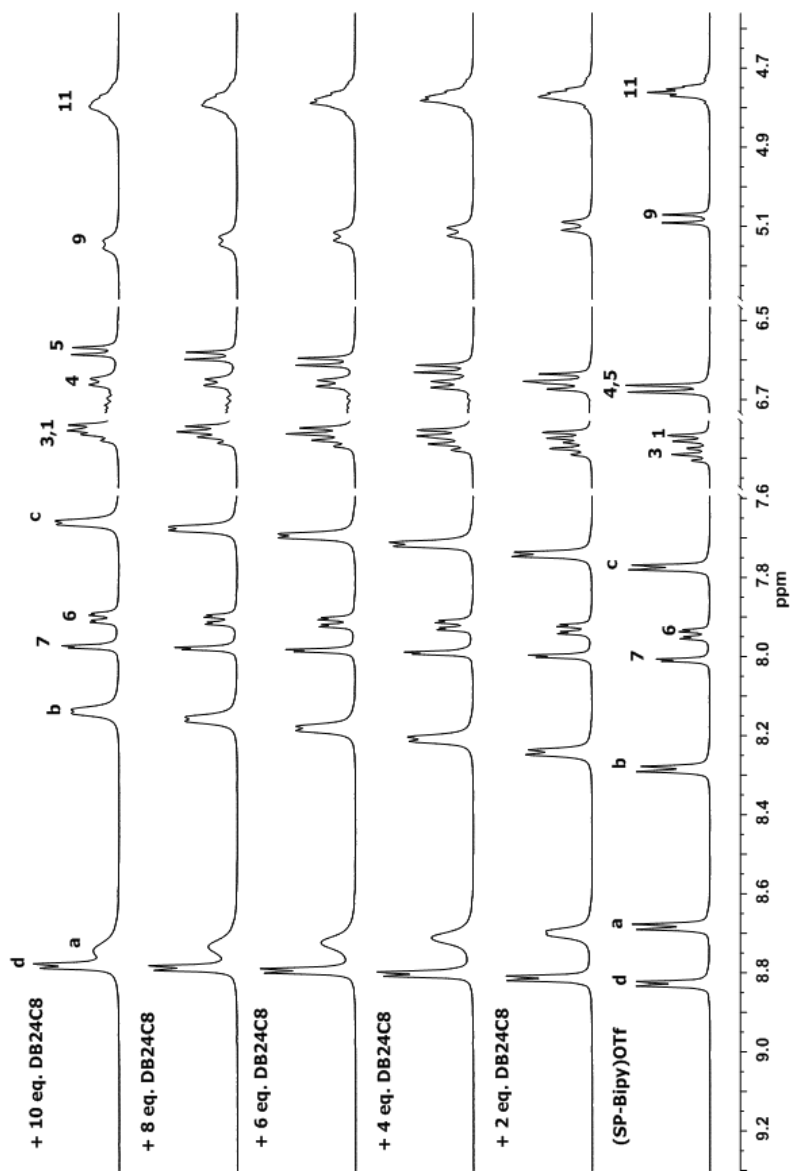


Fig. S26. ^1H NMR spectra of $[\text{SP-Bipy}][\text{OTf}]$ (22 mM) after addition of increasing amounts of DB24C8 . (CD_3CN , 500 MHz, 298 K)

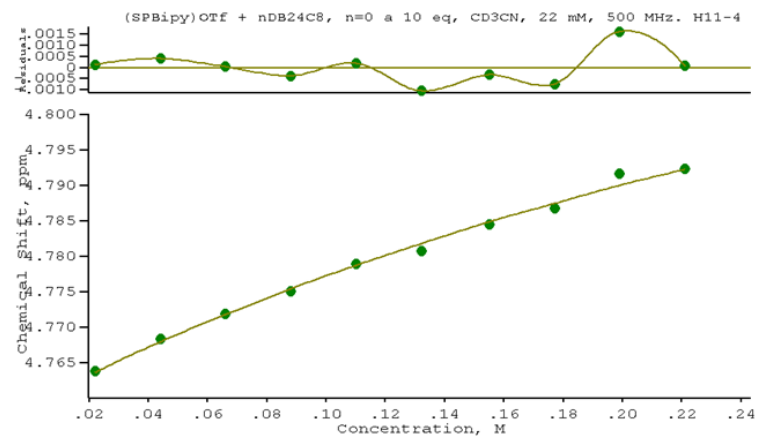
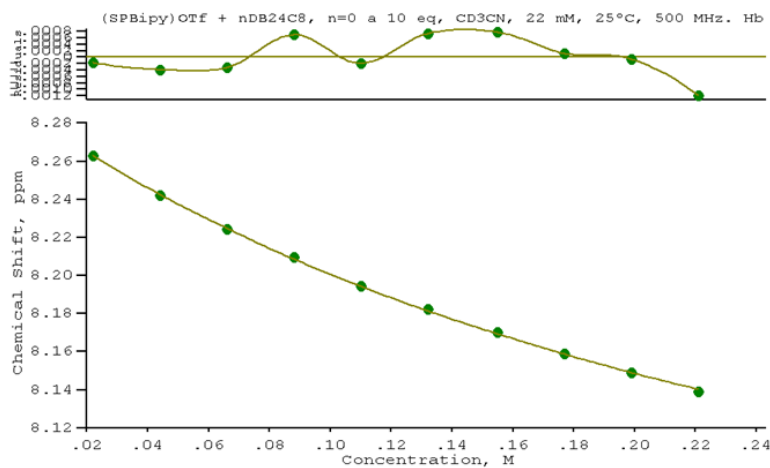
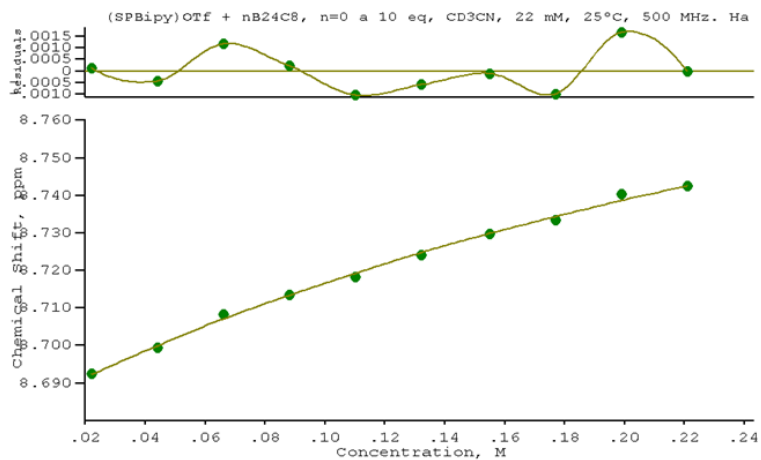


Fig. S27. Change in chemical shift of (top to bottom) H_a, H_b and H₁₁ in [SP-Bipy][OTf] (22mM, CD₃CN) after addition of increasing amounts of DB24C8

2.3. ^1H NMR titration experiment between $[\text{MEH-Bipy-H}][\text{OTf}]_3$ and DB24C8 in CD_3CN

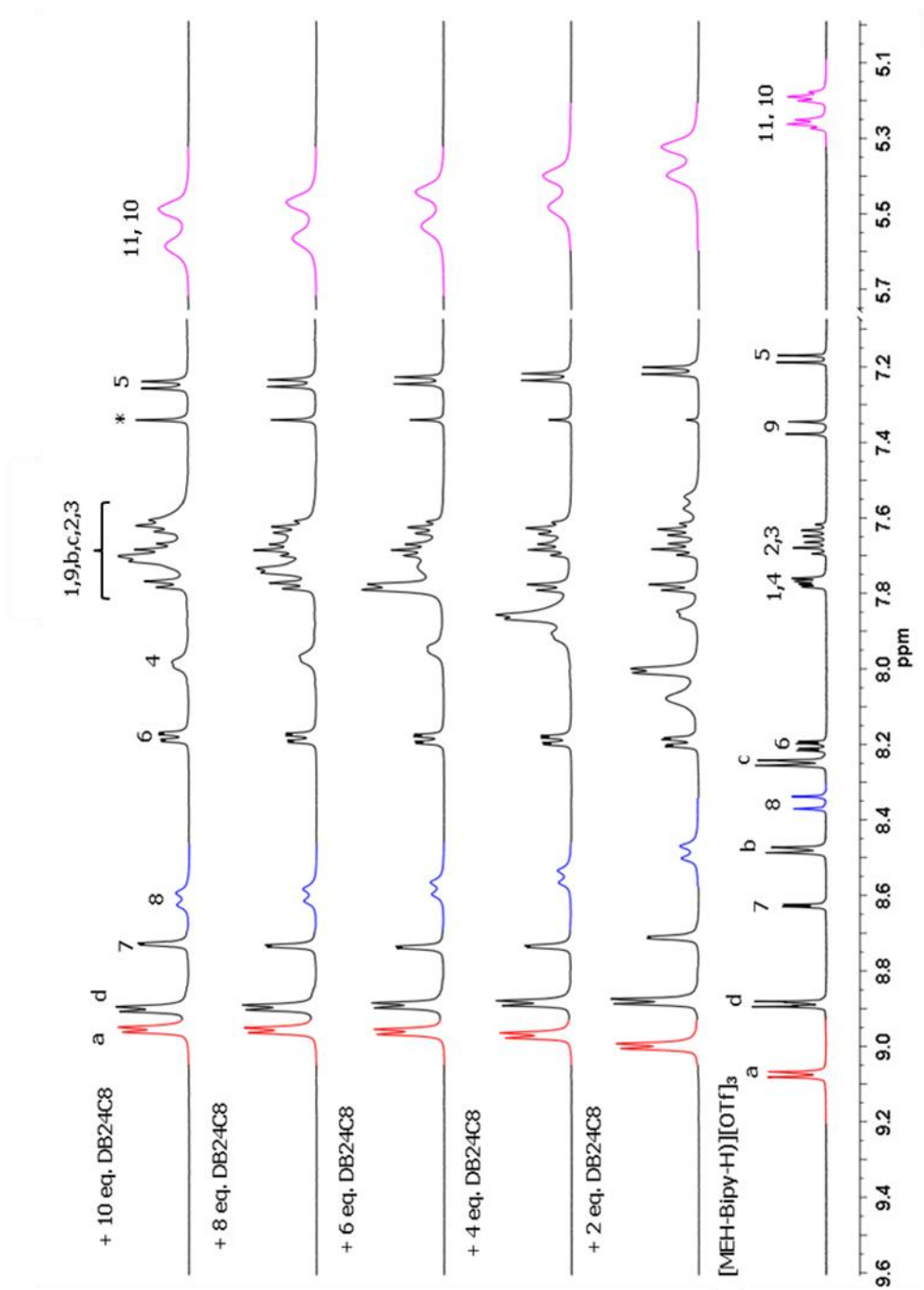


Fig. S28. ^1H NMR spectra of $[\text{MEH-Bipy-H}][\text{OTf}]_3$ (22 mM) after addition of increasing amounts of DB24C8. (CD_3CN , 500 MHz, 298 K)

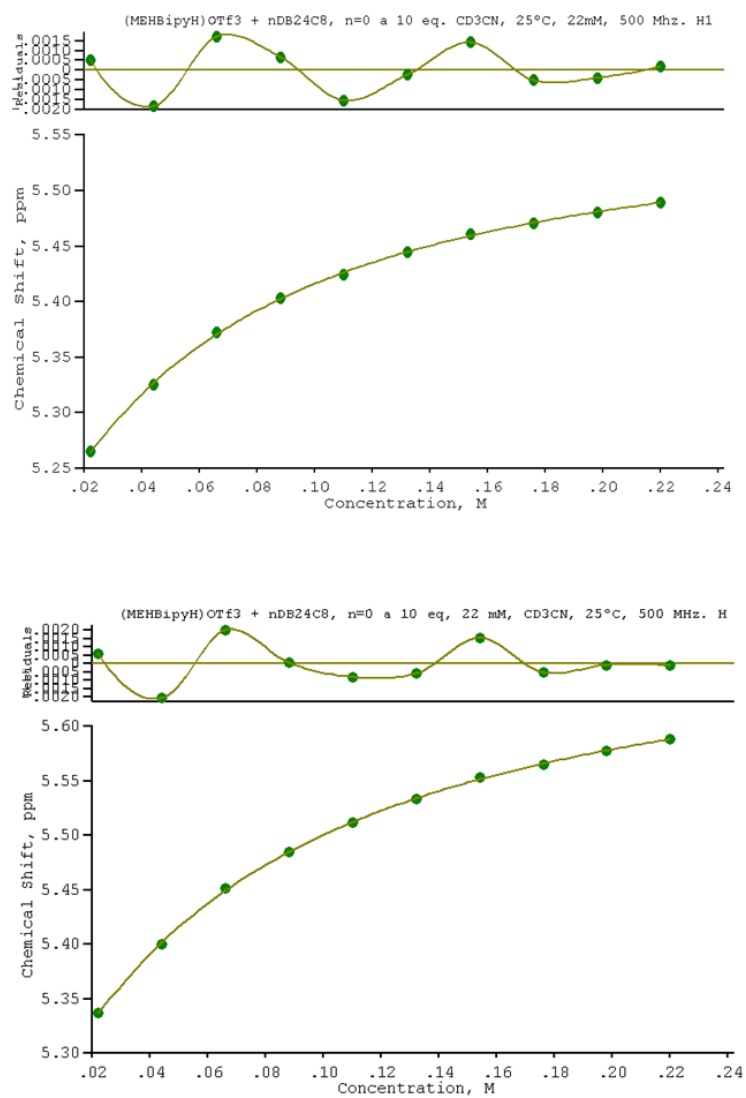


Fig. S29. Change in chemical shift of H₁₀ (top) and H₁₁ (bottom) in [MEH-Bipy-H][OTf]₃ (22mM, CD₃CN) after addition of increasing amounts of DB24C8

2.4. Characterization of [2]*pseudorotaxane* complex formed between [MEH-Bipy-Bn]³⁺ and DB24C8

Proton assignment was confirmed by analysis of 2D T-ROESY NMR experiment.

[2]*Pseudorotaxane* [(MEH-Bipy-Bn)·DB24C8][OTf]₃; δ_{H} (500 MHz, CD₃CN, 298 K): 8.94 (2H, d, ³J_{a',b'} 6.2, H_{a'}), 9.01 (2H, d, ³J_{d',c'} 6.2, H_{d'}), 8.87 (1H, d, ⁴J_{7',6'} 2.5, H_{7'}), 7.84 (H_{b'}), 8.82 (1H, d, ³J_{8',9'} 16.3, H_{8'}), 8.08 (H_{c'}), 8.17 (H_{6'}), 7.85 (H_{1'}), 8.19 (H_{4'}), 7.72 (H_{2'}, H_{3'}), 7.51 (H_{f'}), 7.96 (1H, d, ³J_{9',8'} 16.3, H_{9'}), 7.23 (1H, d, ³J_{5',6'} 9.2, H_{5'}), 6.59 (8H, m, H_{Ar'-DB24C8}), 5.84 (s, H_{e'}), 5.85 (m, H_{11'}), 5.72 (2H, m, H_{10'}), 4.16 (H _{α' -DB24C8}), 3.89 (H _{α' -DB24C8}), 3.68 (H _{β' -DB24C8}), 3.48 (8H, m, H _{γ' -DB24C8}), 1.89 (6H, s, H_{Me}).

HR-MS (ESI-TOF): [(MEH-Bipy-Bn)(DB24C8)(OTf)₂]⁺; (C₆₃H₆₇F₆N₄O₁₇S₂)⁺, *m/z* calculated: 1329.3841 amu, *m/z* found: 1329.3850 amu, error: 0.7 ppm.

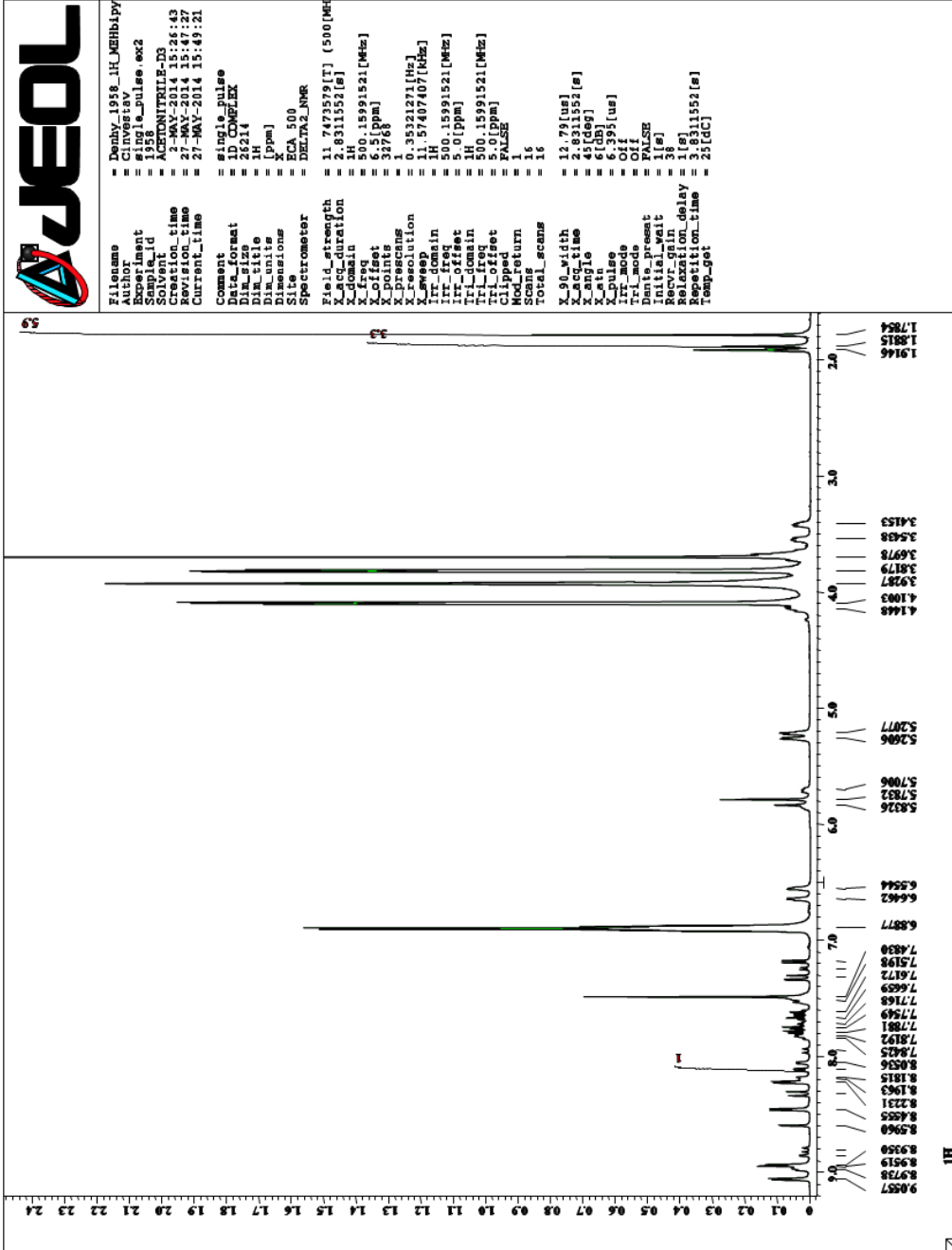


Fig. S30. Full ¹H NMR spectrum of a mixture of [MEH-Bipy-Bn][OTf]₃ (22 mM) and 3 equiv. of DB24C8 (CD₃CN, 500 MHz, 298 K)

+TOF MS: 0.120 to 0.137 min from DH-031012-DHM-4-07.wiff Agilent, subtracted (1.110 to 1... Max: 3.7e5 counts.

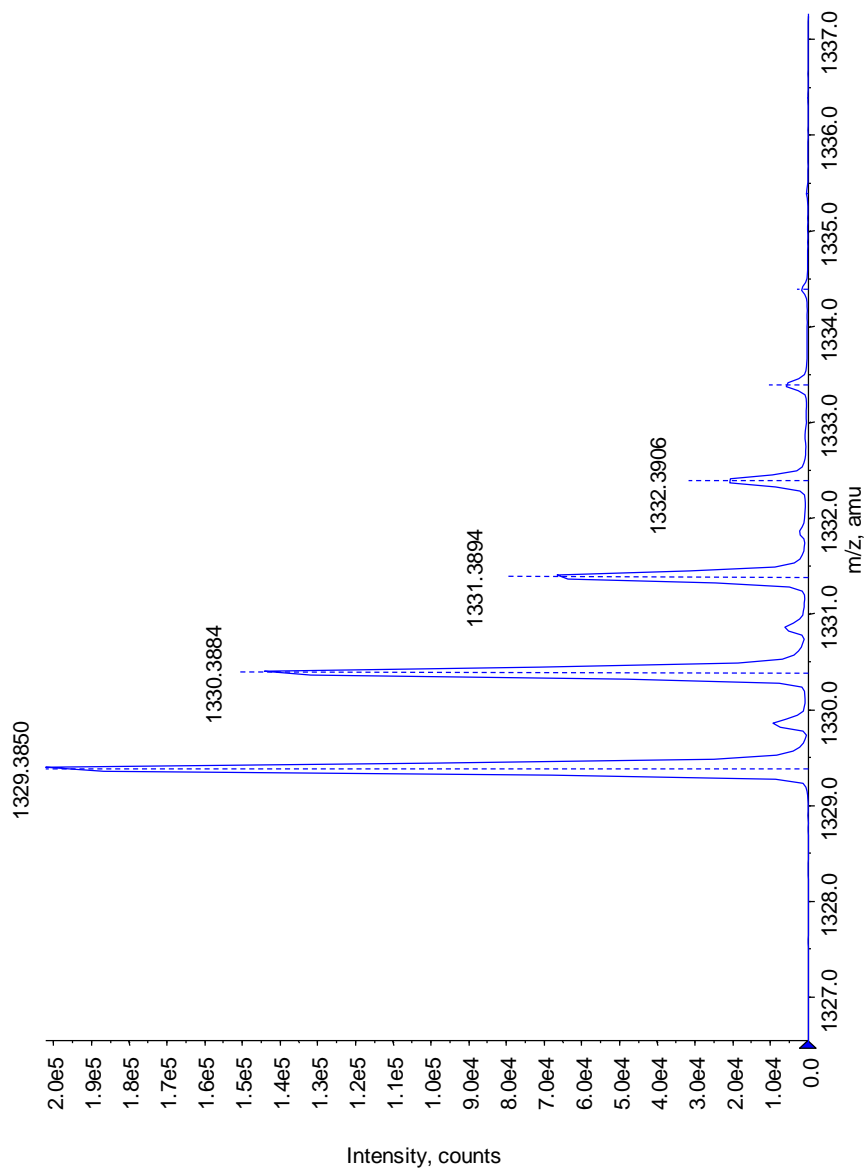


Fig. S31. HR-MS (ESI-TOF) spectrum of [(MEH-Bipy-Bn)(DB24C8)(OTf)₂]⁺, (C₆₃H₆₇F₆N₄O₁₇S₂)⁺

3. Exchange rate constant determination for the threading-dethreading motion between [MEH-Bipy-Bn][OTf]₃ and DB24C8

Exchange rate constant (k) was estimated by 2D T-ROESY NMR experiment recorded on a 500 MHz spectrometer at 298 K with $\tau_m = 1$ sec, using the equations (1) and (2).⁵ I_{AA} and I_{BB} are the diagonal peak intensities; I_{AB} and I_{BA} are the cross-peak intensities.

An equimolar solution of [MEH-Bipy-Bn][OTf]₃ with DB24C8 (0.1 M) in CD₃CN was used for this experiment.

The estimated value of the exchange rate constant was 1.18 s⁻¹.

$$r = \frac{I_{AA} + I_{BB}}{I_{AB} + I_{BA}} \quad \dots (1)$$

$$k = \frac{1}{\tau_m} \ln \frac{r + 1}{r - 1} \quad \dots (2)$$

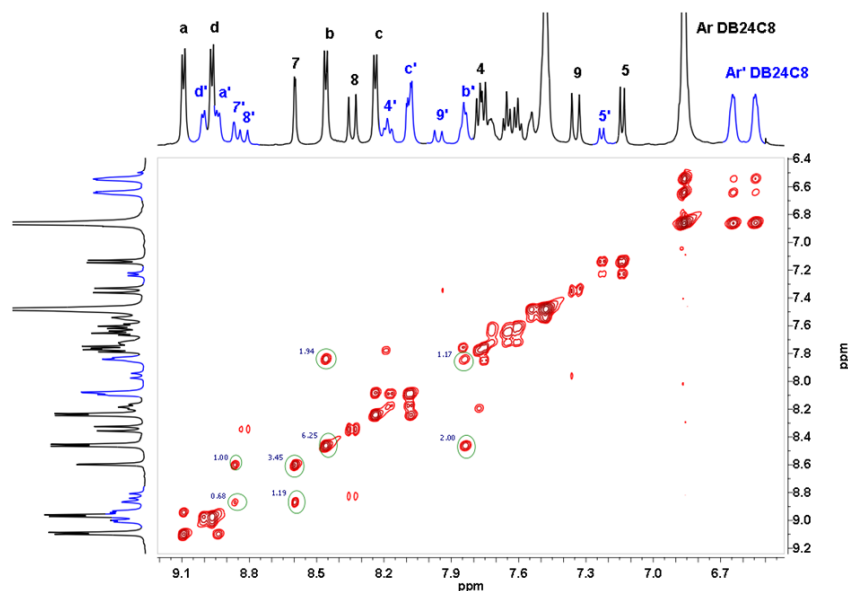


Fig. S32. 2D T-ROESY NMR experiment of an equimolar mixture of [MEH-Bipy-Bn][OTf]₃ and DB24C8 (0.1 M, CD₃CN, 298 K). Diagonal peak intensities and cross-peak intensities of signals corresponding to H₇ and H_b are shown.

4. UV-Vis titration experiment between [MEH-Bipy-Bn][OTf]₃ and DB24C8 in CH₃CN

A stock solution of [MEH-Bipy-Bn][OTf]₃ (2 mM) was prepared by dissolving 8.8 mg (0.01 mmol) of [SP-Bipy-Bn][OTf]₂ and 3 μ L of HOTf (0.03 mmol) in 5 mL of dry CH₃CN. After maintaining acidic solution in the dark overnight (to achieve completion of the isomerization process into the merocyanine isomer), a 0.025 mM solution was prepared by dilution in the absence of light. 2 mL of this solution were placed into a quartz cell (path length: 1 cm). Then, increasing amounts of **DB24C8** were added to the cell (using a 5 mM solution in CH₃CN) and electronic spectra were collected.

The absorbance of the band corresponding to the protonated guest was followed (422 nm). There are no significant changes in the absorbance neither in the position of the band after addition of the macrocycle.

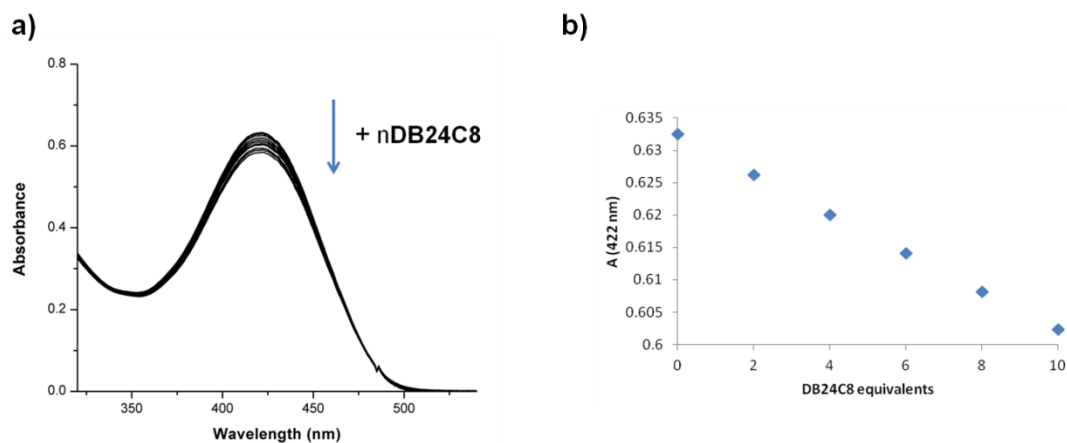


Fig. S33. UV-Vis titration experiment of a [MEH-Bipy-Bn][OTf]₃ solution (0.025 mM) with increasing amounts of **DB24C8** (CH₃CN, 298 K). **a)** Partial UV-Vis spectra showing the absorption band corresponding to [MEH-Bipy-Bn][OTf]₃ (422 nm) after addition of the macrocycle. Top spectrum corresponds to the initial point of the titration; bottom spectrum corresponds to the final point (after addition of 10 equivalents of **DB24C8**). **b)** Change in the absorbance of the band at 422 nm after addition of increasing amounts of **DB24C8**.

5. Estimation of ϵ for zwitterionic species **[ME-Bipy]⁺** by deprotonation of **[MEH-Bipy-H][OTf]₃**

Photoconversion yield of **[SP-Bipy][OTf]** into **[ME-Bipy][OTf]** was obtained by the estimation of the ϵ value corresponding to the zwitterionic species **[ME-Bipy]⁺** at 582 nm. The procedure used is described below.

A stock solution of **[MEH-Bipy-H][OTf]₃** (2 mM) was prepared from dissolving 6.4 mg (0.01 mmol) of **[SP-Bipy][OTf]** and 3 μ L of HOTf (0.03 mmol) in 5 mL of dry CH₃CN. After maintaining acidic solution in the dark overnight (to achieve completion of the isomerization process into the merocyanine isomer), solutions at lower concentrations were prepared by dilution in the absence of light (0.04, 0.03, 0.02, 0.01 and 0.008 mM respectively).

2 mL of each solution were placed into a quartz cell (path length: 1 cm). After recording an absorption spectrum at 293 K, 10 equiv. of pyridine (using a 0.08 mM solution in CH₃CN) were added as a base; immediately another spectrum was collected.

Considering a complete deprotonation of the **MEH** species; we hypothesized that the concentration of the zwitterion **[ME-Bipy]⁺** obtained *in situ*, is practically the same than the concentration of the initial solution of **[MEH-Bipy-H]³⁺** used.

We plotted the absorbance observed at 582 nm vs the apparent concentration of **[ME-Bipy]⁺** to obtain a linear fitting of the data. Considering Lambert-Beer's law, the slope corresponds to absorption coefficient.

$$A(582 \text{ nm}) = \epsilon[\text{ME}]$$

The absorption coefficient estimated by this method was 31082 cm⁻¹M⁻¹.

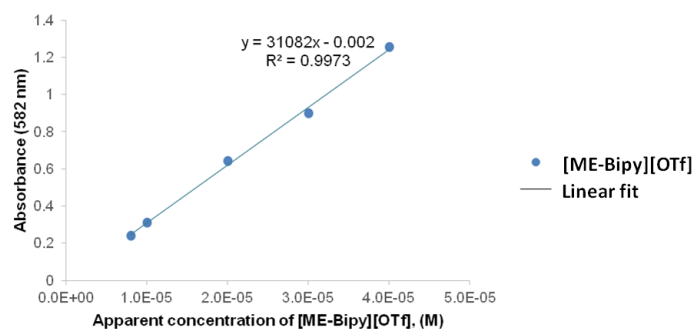
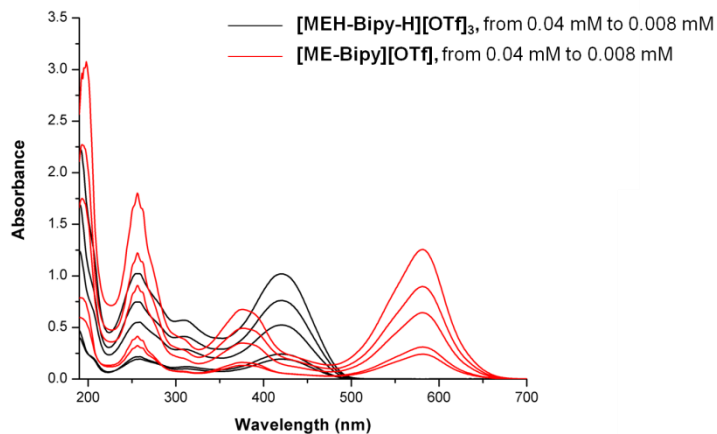


Fig. S34. Estimation of ϵ at 582 nm for the zwitterionic species **[ME-Bipy]⁺** from deprotonation of **[MEH-Bipy-H][OTf]₃** with pyridine (CH₃CN, 293 K) by UV-Vis spectroscopy. Electronic spectra at each concentration before and after base addition (top) and linear fitting of the data (bottom) are shown.

6. Synthesis of [2]Rotaxane complex induced photochemically by pseudorotaxane formation between [ME-Bipy]⁺ and DB24C8

30 mg (0.047 mmol) of [SP-Bipy][OTf], 106 mg (0.24 mmol) of DB24C8 and 44 μ L (0.24 mmol) of 4-tertbutylbenzyl bromide, as end-capping agent, were dissolved in 0.5 mL of CD₃CN and poured into a Suprasil® quartz NMR tube. This solution was irradiated with UV light (254 nm) for 18 h at 30 °C, to obtain [ME-Bipy]⁺ *in situ* and promote pseudorotaxane formation followed by capping. A precipitated is formed and filtered. The filtrate was recovered; HR-MS of this solution show evidence of the presence of a [2]rotaxane complex.

HR-MS (ESI-TOF): [(ME-Bipy-Bn)(DB24C8)(OTf)]⁺; (C₆₆H₇₄F₃N₄O₁₄S)⁺, *m/z* calculated: 1235.4869 amu, *m/z* found: 1235.4852 amu, error: 1.4 ppm.

7. References

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