Electronic Supplementary Material (ESI) for ChemComm.
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A Highly – Ordered Rigid Multichromophoric 3D Supramolecular Network by Combining Ionic and Coordination – Driven Self - Assembly

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Materials and Methods: All chemicals were used without further purification and purchased from commercial sources as follows: 4-ethynylpyridine hydrochloride (Aldrich), tert-butyllithium2.0 M in hentane (Aldrich), 2,4-dimethylpyrrole (Aldrich), 3,5-Di-tert-butylbenzoic acid (Aldrich), boron trifluoride diethyl etherate (Aldrich), 1,3-bis(diphenylphosphino)propane (dppp) (Acros Organics).Pt(dppp)(OTf)$_2$was prepared according to literature procedures.[1] 3,5-di-tert-butylbenzoyl chloride from the corresponding acid with $SOCl_2$ at rt for 2 h.1,3,6,8-pyrenetetrasulfonic acid tetrasodium salt (Aldrich) was converted to the tetrabutylammonium salt of**4SPy**$^{-4}$ with tetrabutylammonium hydroxide in CH_2Cl_2, then washed with water until neutral pH.

Solvents were purified as follows: CH_2C1_2, $CHCl_3$, $ClCH_2CH_2Cl$, CH_3CN were distilled over CaH_2. DMF was dried with CaH_2 and distilled under reduced pressure. THF was distilled over Na / benzophenone under Ar. $CDC1_3$ was stirred with $K_2CO_3$for 12 h and distilled.DMF-d7 was used without further purification.

NMR spectra were recorded on a Bruker Avance DRX 500 spectrometer. ^1H,^{13}C chemical shifts are reported relative to residual solvent signals, and$^{31}P\{^1H\}$ chemical shifts are referenced to an external 85% H_3PO_4 (δ 0.00 ppm) sample. DOSY NMR experiments were carried out with solutions of 4 cm height to ensure gradient linearity along the samples. The temperature was controlled with air flow and kept at 298.0 ± 0.1 K. Data were acquired with 32 scans for each gradient step, 4 dummy scans and a linear gradient of 32 steps between 2% and 95%. Processing was carried out with Bruker's Topspin 2.1 software.

Absorption spectra were recorded on a Perkin-Elmer Lambda-16 spectrophotometer. Steady-state fluorescence spectra were performed by Perkin-Elmer model LS-50B and Edinburgh Instruments model FS-900 spectrophotometers. Fluorescence lifetimes (τ) were determined using the time correlated single-photon counter FL900, of the Edinburgh Instruments spectrophotometer. Fluorescence quantum yield measurements of the Bodipy-based compounds in 1,2-dichloroethane ($\eta(ClCH_2CH_2Cl) = 1.4448$) were obtained relative to Rhodamine 6G in ethanol (Φ=0.94, $\eta(EtOH) = 1.358$)[2]. The quantum yield of the pyrene's derivative was measured relative to an aqueous solution of quinine sulphate containing 1N H_2SO_4 ($\Phi = 0.546$)[3].

All measurements were carried out by keeping the concentration of the metallosupramolecular assembly **3**$^{+4}$ constant at 0.20 mM, owing to the fact that below this concentration threshold partial disintegration of **3**$^{+4}$ was observed.

The fluorescence dynamics in the fs to ps timescale were obtained using a femtosecond time resolved upconversion system described in details elsewhere.[4,5]All measurements were carried out in DMF solutions of **3**$^{+4}$ (0.2 mM) in the presence of 0.4 equiv. (R = 0.4) of **4SPy**$^{-4}$ to prevent the formation of highly insoluble infinite polymeric chains.

The fundamental beam of a mode-locked Ti:Sapphire laser at 760nm with 80fs pulse duration has been frequency doubled through a BBO crystal. The second harmonic, at 380nm, was used for the excitation of the samples while the fundamental beam was used as the gate beam. The excitation power was typically below 6mW. For avoiding thermal degradation, the samples were placed in a rotating holder. The fluorescence of the samples and the gate beam were focused on a second BBO crystal to generate an upconversion beam (type I phase matching). This beam passed through appropriate filters and a monochromator and it was detected through a photomultiplier. The Instruments's Response Function (IRF) of the technique was ~140fs. The polarization plane of the excitation beam was changed with respect to that of the detection by means of a Berek compensator. Measurements were performed under magic angle conditions while for determining the time dependent anisotropy, the fluorescence decays polarized parallel and perpendicularly to the excitation polarization plane were also measured. Then the fluorescence anisotropy was determined from the equation

$$r(t) = \frac{I_{par} - I_{per}}{I_{par} + 2I_{per}} \quad (1)$$

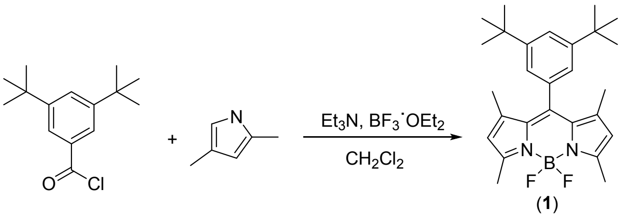
Fitting of the magic angle dynamics was carried out by using a multi-exponential trial-function convoluted with the IRF, which is considered to have a Gaussian shape. The time resolved anisotropy parameters were determined by fitting the difference factor $I_{par} - I_{per}$ (difference fit).

From equation (1)

we obtain $r(t) = \frac{I_{par} - I_{per}}{I_{par} + 2I_{per}} \Rightarrow r(t) = \frac{I_{par} - I_{per}}{I_{magic}} \Rightarrow I_{par} - I_{per} = r(t) \cdot I_{magic}$. Therefore, for obtaining the anisotropy parameters, the fitting function of the magic angle dynamics (with fixed parameters) was multiplied by the anisotropy fitting function (single or bi-exponential) and convoluted with the IRF. The final function was fitted to the $I_{par} - I_{per}$ experimental results. In fitting the anisotropy dynamics, a lifetime of 0.95 ps was found for the EET from **4SPy**$^{-4}$ to **3**$^{+4}$. This is considered as an average of the two lifetimes found in magic angle dynamics, not resolved in time dependent anisotropy because of the decreased signal to noise ratio of the difference factor.

Electrospray ionization mass spectrometry (ESI-MS) was performed in the positive ionization mode on a TripleTOF 5600+ mass spectrometer (Sciex, Toronto, Canada) equipped with a DuoSpray ion source. The spray voltage was set to 3.7 kV. Gas flows of 5 arbitrary units for the nebulizer gas and 10 arbitrary units for the turbo gas were employed. The temperature of the turbo gas was set to 25 °C. Samples were dissolved in DMF/acetone (1/1) and 100 µg/ml solutions were infused at a flow rate of 5.0 µl/min. The instrument was controlled by the Analyst TF 1.6 software (Sciex).

Synthesis of Bodipy 1.



(**1**)

2,4-dimethylpyrrole (4.67 mmol, 480 µL) was added to a stirred, degassed solution of 3,5-di-tert-butylbenzoyl chloride(2.13 mmol, 540 mg) in 45 ml of anhydrous CH_2Cl_2 held at room temperature. The mixture was stirred at rt for 3 d. Et_3N (12.84 mmol, 1.79 mL), $BF_3 \cdot OEt_2$ (17.1mmol, 2.11 mL) were added and the mixture was subsequently stirred at rt for 24 h under Ar. Water was added, and the solution was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and concentrated under vacuum to give a dark red solid. The solid was treated with $NaBH_4$ (0.26 mmol, 10 mg) inboilingEtOH for 1h. Hot filtration followed and the solution was concentrated under vacuum to give a red solid which was purified by column chromatography. Yield: 25%.^{1}H NMR ($CDCl_3$): δ 7.48 (s, 1H), δ 7.12 (s, 2H), 5.98 (s, 2H), 2.56 (s, 6H), 1.37 (s, 6H), 1.33 (s, 18H); ^{13}C NMR ($CDCl_3$): 155.2, 152.1, 143.4, 143.3, 134.2, 131.7, 122.2, 122.0, 121.1, 35.2, 31.5, 14.7, 14.2; Anal. Calcd for $C_{27}H_{35}BF_2N_2$: C, 74.31; H, 8.08; N, 6.42. Found: C, 74.48; H, 7.93; N, 6.56;

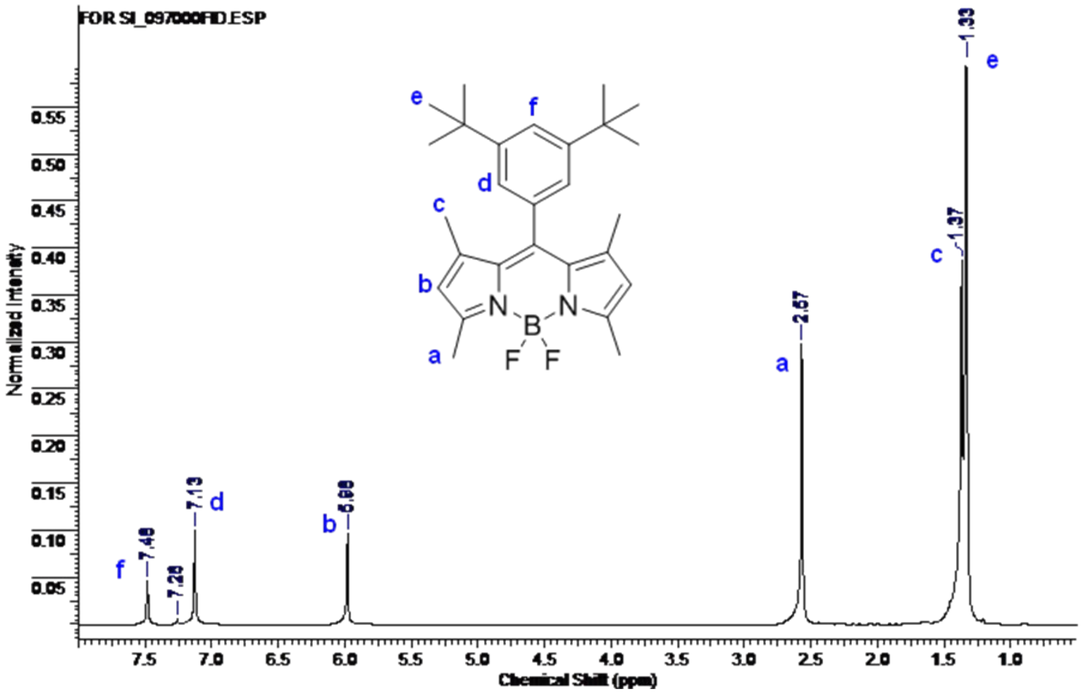
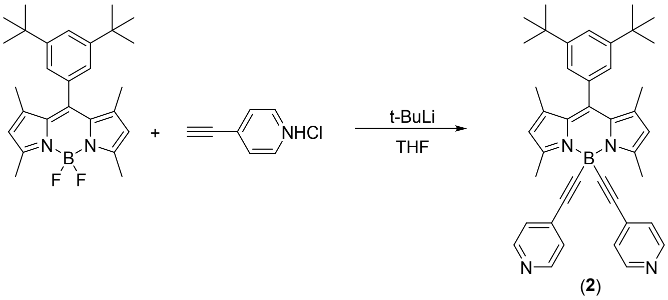


Figure S1. ^{1}H NMR (500 MHz) spectrum of **1** in $CDCl_3$.

Synthesis of Bodipy 2.



In a Schlenk flask, tert-butyllithium (680μl, 1.36mmol) was added dropwise at -78 °C to a stirred solution of 4-ethynylpyridine hydrochloride (140.0 mg, 1.36 mmol)in 5 ml of anhydrous THF under Ar. The mixture was stirred at -78°C for 20 min and at room temperature for another 1.5 h. The precursor **Bodipy1** (142.0 mg, 0.325mmol) was dissolved in 15 ml of anhydrous THF under Ar and added to the lithium acetylide mixture through a pressure equalising dropping funnel. After 24 hthe reaction was stopped with water, extracted with $CH_2Cl_2$and washed 3 times with water. The organic layer was dried with Na_2SO_4, filtered, and after evaporation of the solvents purified by silica gel column chromatographywithEtOAc as eluent. Recrystallization from EtOAc gave 117 mg (0.194mmol) of bright orange crystals (Yield 60%).^{1}H NMR ($CDCl_3$): δ 8.49 (d, J=4.3 Hz, 4H, Ha-Py), δ 7.48 (s, 2H), 7.16 (s, 2H), 6.11 (s, 2H), 2.84 (s, 6H), 1.39 (s, 6H), 1.33 (s, 18H); ^{13}C NMR ($CDCl_3$):154.9, 151.9, 149.4, 143.6, 141.8, 134.1, 133.2, 129.7, 125.7, 122.2, 121.8, 121.5, 35.1, 31.4, 16.0, 14.3; Anal. Calc. for $C_{41}H_{43}BN_4$: C, 81.72; H, 7.19; N, 9.30. Found: C, 82.06; H, 7.15; N, 9.23;

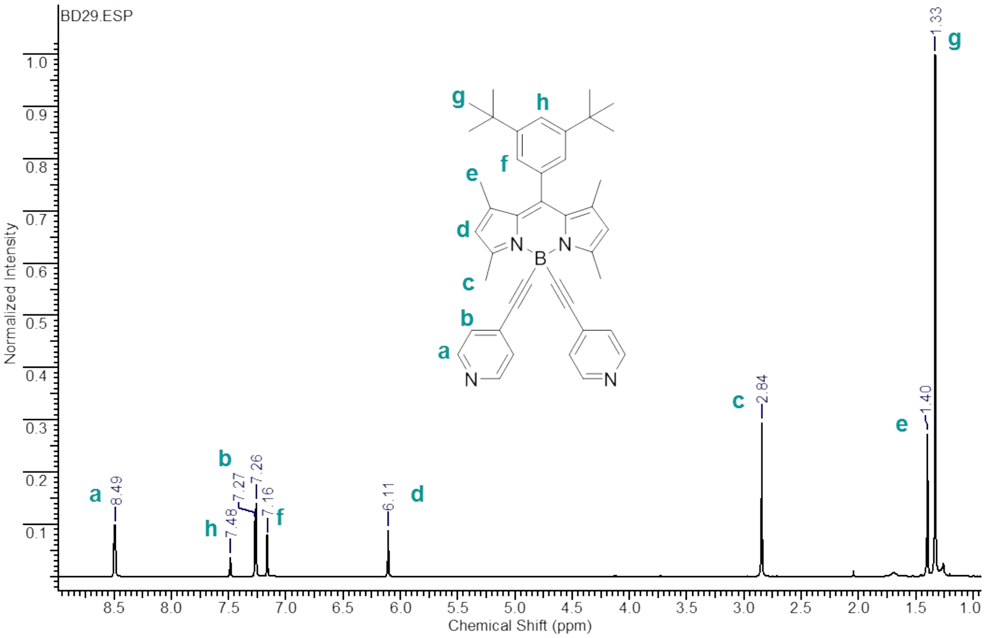


Figure S2. ^{1}H NMR (500 MHz) spectrum of **1** in $CDCl_3$.

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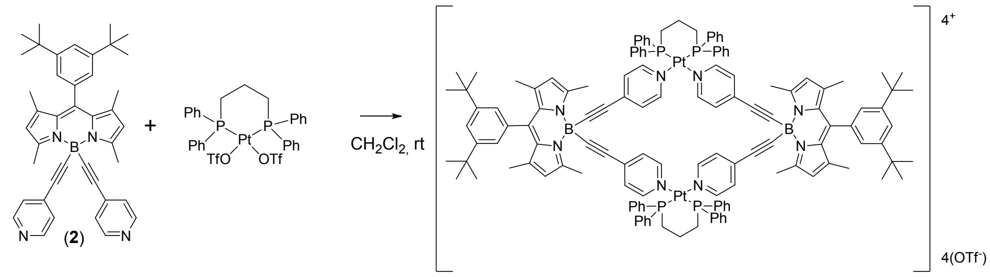
Self-assembly of Rhomboidal Cavitand 3(OTf)$_4$**.**



18.9 mg (0.031mmol) of (**2**) were dissolved in 2.5 ml of CH_2Cl_2 a 20 ml vial. 28.4 mg (0.031mmol) of Pt(dppp)(OTf)$_2$ were added to the vial with continuous stirring at rt. Microcrystalline solidwas obtained when the volume of the solution was reduced to 1 ml with a stream of Ar, followed by slow diffusion of 2-methyl butane. The solid was washed twice with Et_2O and dried for 8 hours with an oil pump. Yield 86 % (40.6 mg or 0.0135mmol). ^{1}H NMR ($CDCl_3$): δ8.76 (d, J=5.4 Hz, 8H), 7.62 (bs,16H), 7.49 (s, 2H), 7.35 (bs, 24H), 7.11 (s, 4H), 6.85 (d, J=6.0 Hz, 8H), 6.13 (s, 4H), 3.23(bs, 8H), 2.62 (s, 12H), 2.21 (b, 4H), 1.40(s, 12H), 1.32 (s, 36H); ^{13}C NMR ($CDCl_3$): 155.4, 152.2, 149.8, 143.7, 142.2, 136.5, 133.8, 133.0, 132.4, 129.7, 129.5, 128.3, 124.1, 122.1, 122.0, 121.8, 92.2, 35.1, 31.4, 17.7, 16.0, 14.4; Anal. Calc. for $C_{140}H_{138}B_2F_{12}N_8O_{12}P_4Pt_2S_4$: C, 55.74; H, 4.61; N, 3.71. Found: C 56.01, H 4.90, N 3.51.ESI-MS *m/z*1358.9219(theoretical: 1358.9275)[M-2OTf]$^{2+}$ and *m/z*856.2906(theoretical: 856.3009)[M-3OTf]$^{3+}$ (see Figure S8).

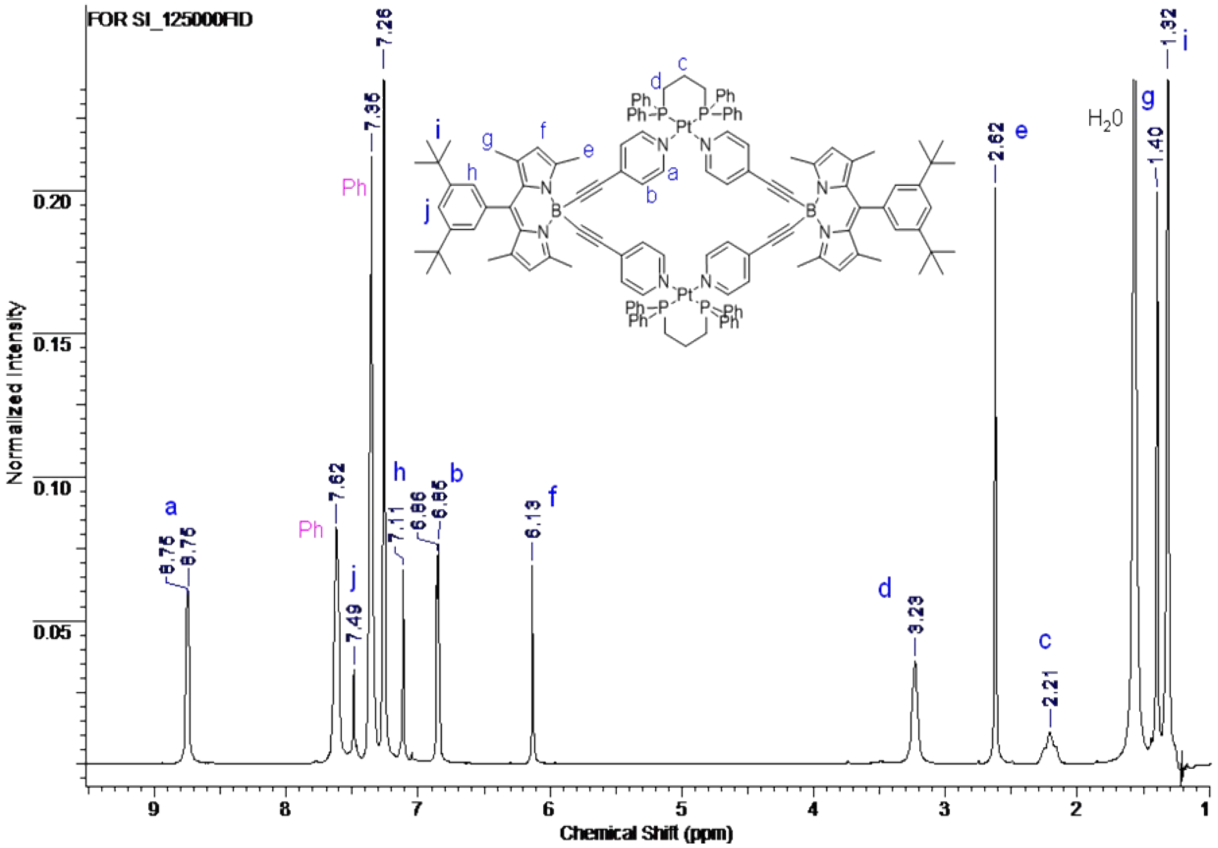


Figure S3. ^{1}H NMR (500 MHz) spectrum of **3**(OTf)$_4$in $CDCl_3$.

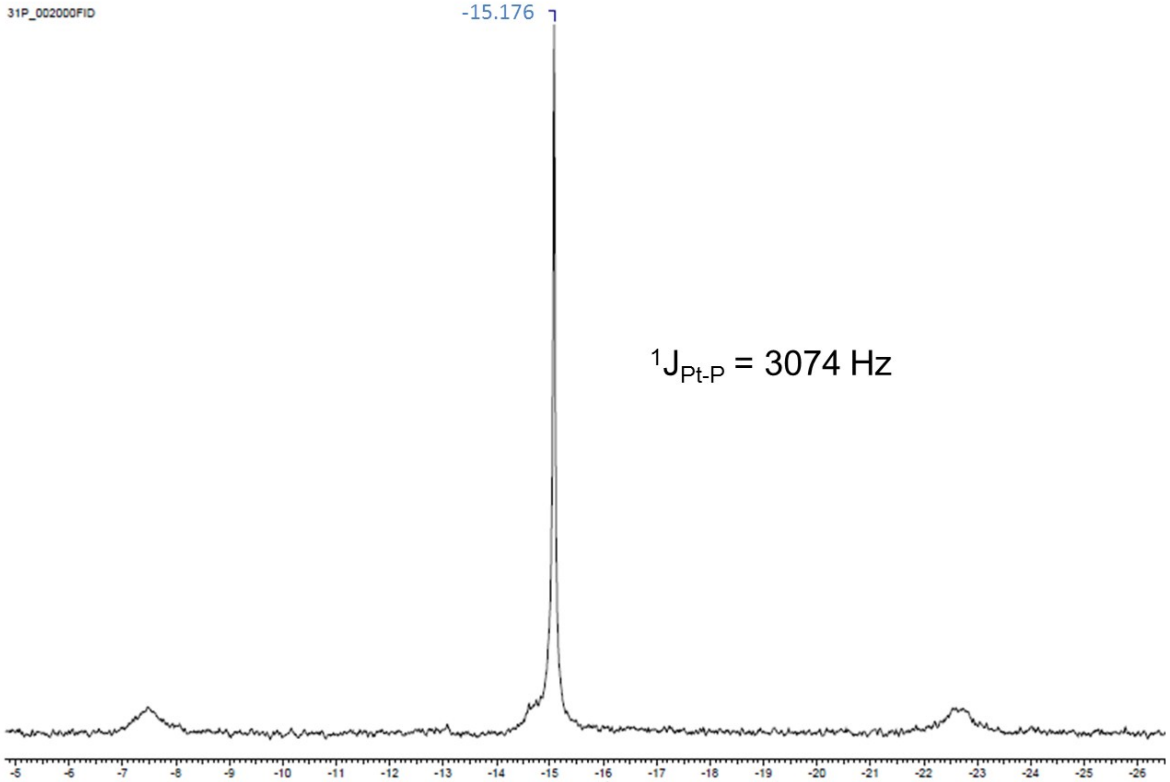


Figure S4. ^{31}P {^1H} NMR (121.4 MHz) spectrum of **3**$(OTf)_4$in $CDCl_3$.

Influence of molar ratio R = [4SPy^{-4}]/[3^{+4}] to ^{1}H NMR shift

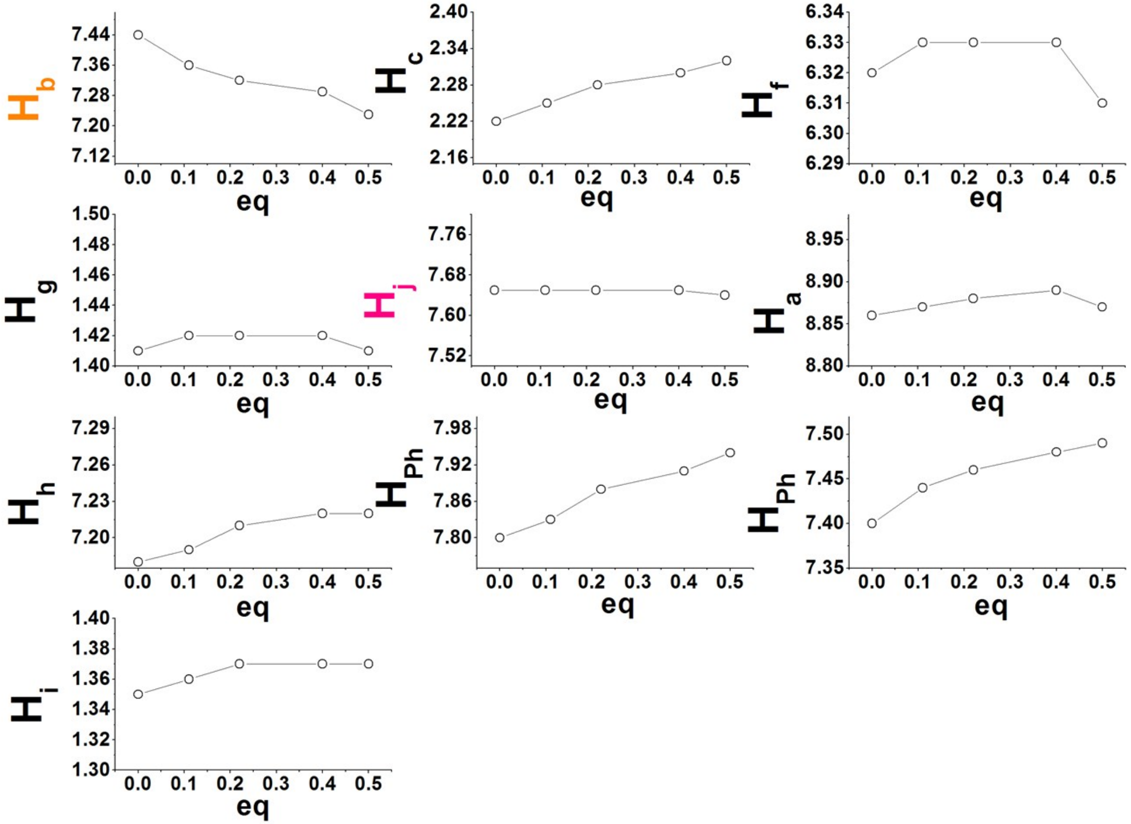


Figure S5. ^{1}H NMR of**3^{+4}**. Chemical shift (ppm) *vs* molar ratio R = [**4SPy^{-4}**]/[**3^{+4}**].

^{1}H DOSY – SPECTRA

For a spherical molecule the diffusion coefficient D is described by the Stokes-Einstein equation: $D = kT/(6\pi\eta r_s)$, where k is the Boltzmann constant, T the temperature, η the viscosity of the solvent and r_s the hydrodynamic radius of the molecule.

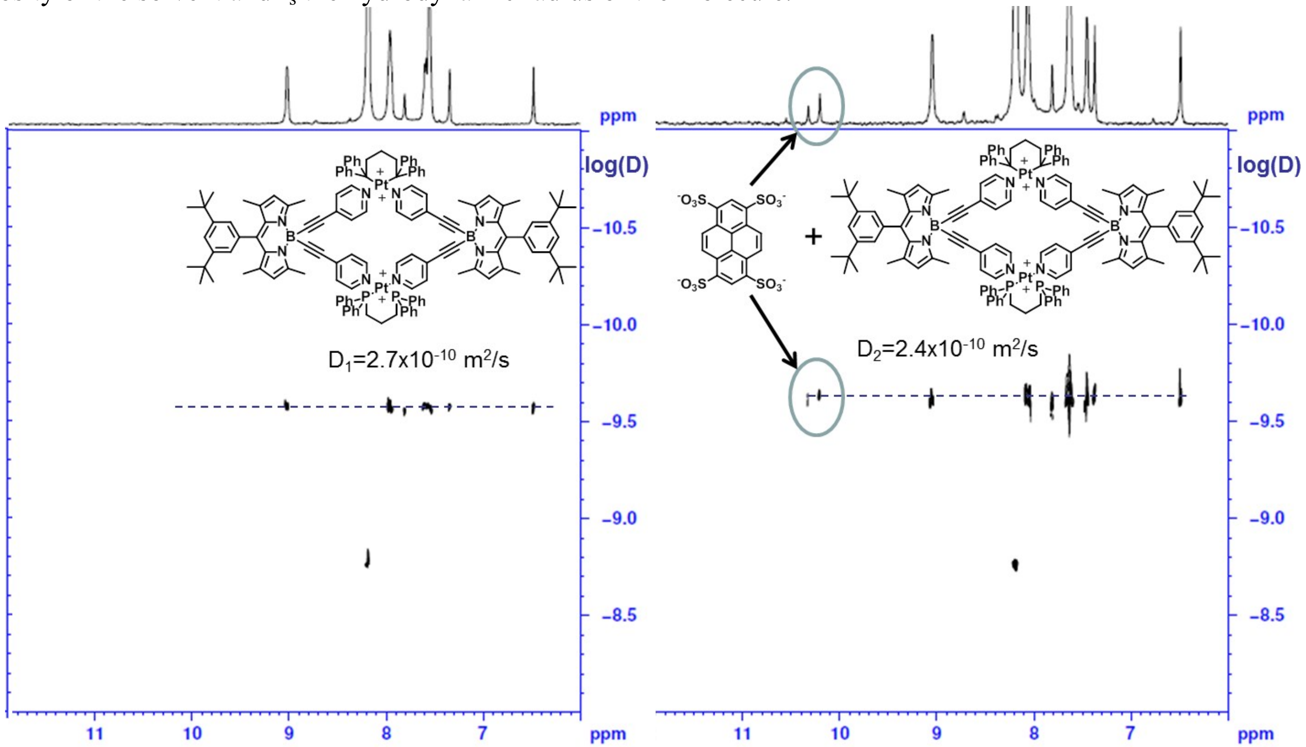


Figure S6.^{1}H DOSY spectra (500 MHz, DMF-*d7*, 298 K) of **3**(OTf)$_4$2x10^{-4} M**(left**) and **3**(OTf)$_4$ 2x10^{-4} M with the addition of **4Spy**(NBu$_4$)$_4$ 8x10^{-5} M (**right**).

DOSY measurements showed that the assembly **3**$^{+4}$is forming adducts anddiffuses together with the guest **4SPy**$^{-4}$. The assembly**3**$^{+4}$wasmoderately influenced by the addition of the guest **4SPy**$^{-4}$and the hydrodynamic radius was increased from 10.0 Å to 11.3 Å indicative of small supramolecular adducts.

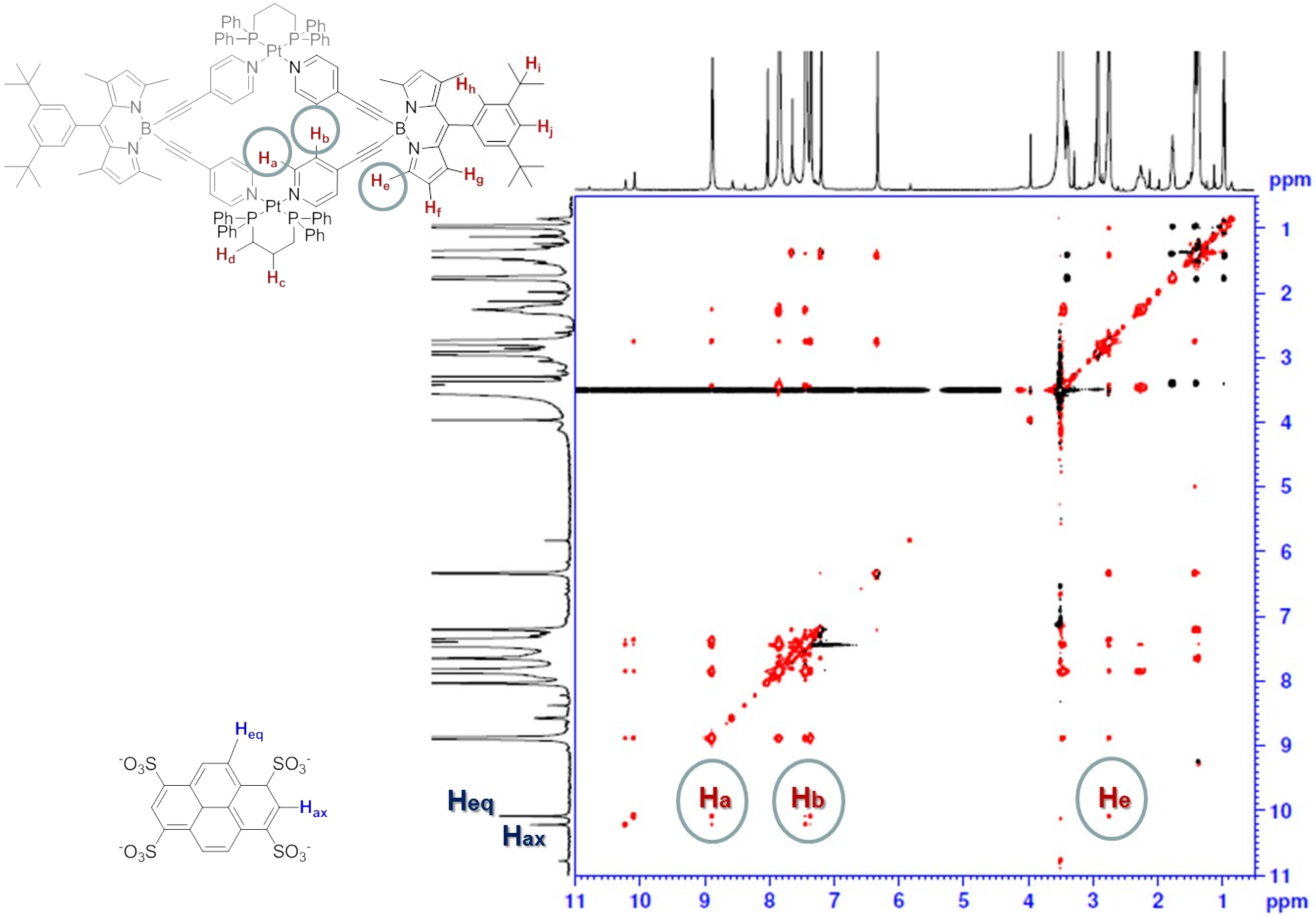


Figure S7. ^{1}H-^{1}H NOESY (500 MHz, DMF-*d7*, 298 K) spectrum of $4\text{x}10^{-4}$ M **3**(OTf)$_4$ and $1.5\text{x}10^{-4}$ M**4Spy**(NBu$_4$)$_4$.

High-resolution electrospray ionization mass spectrometry (ESI –MS)

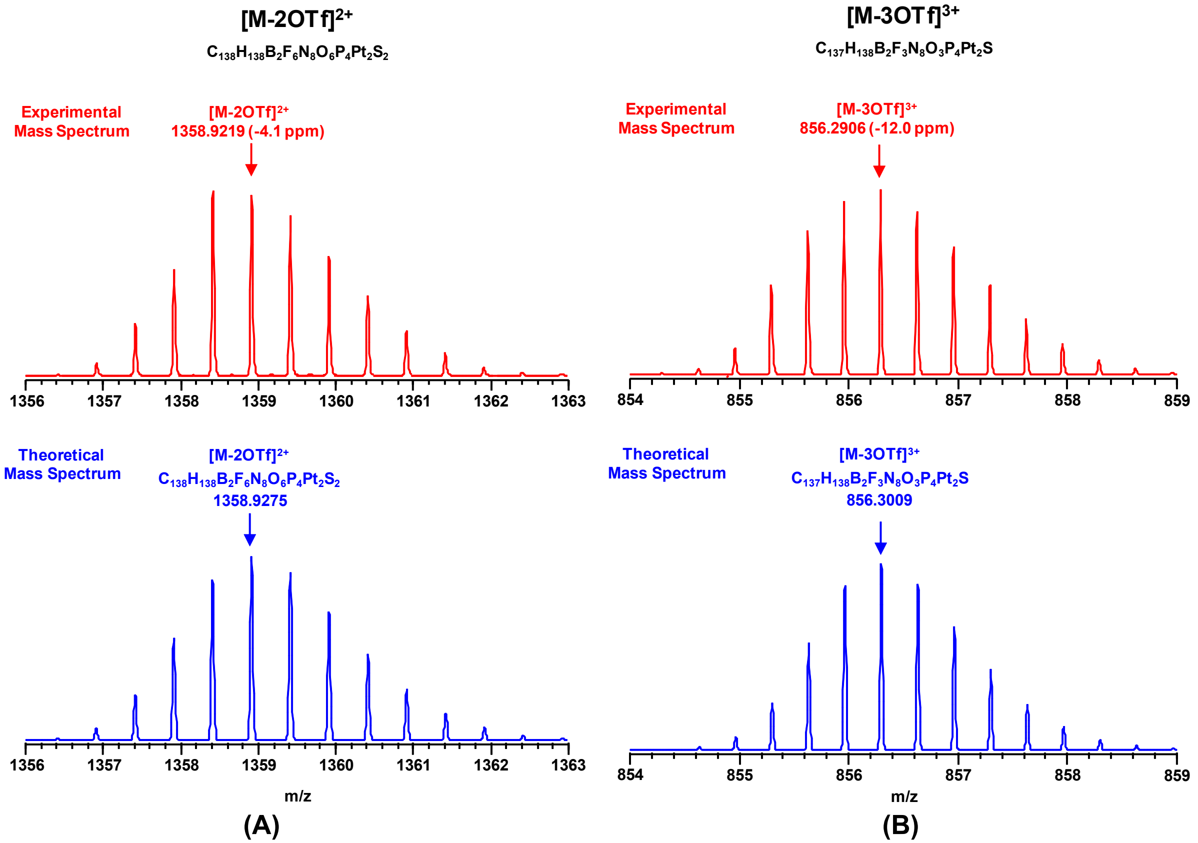


Figure S8. Experimental (red) and theoretical (blue) ESI mass spectra of **(A)** $[\mathbf{3}(\mathrm{OTf})_2]^{2+}$ and **(B)** $[\mathbf{3}(\mathrm{OTf})]^{3+}$.

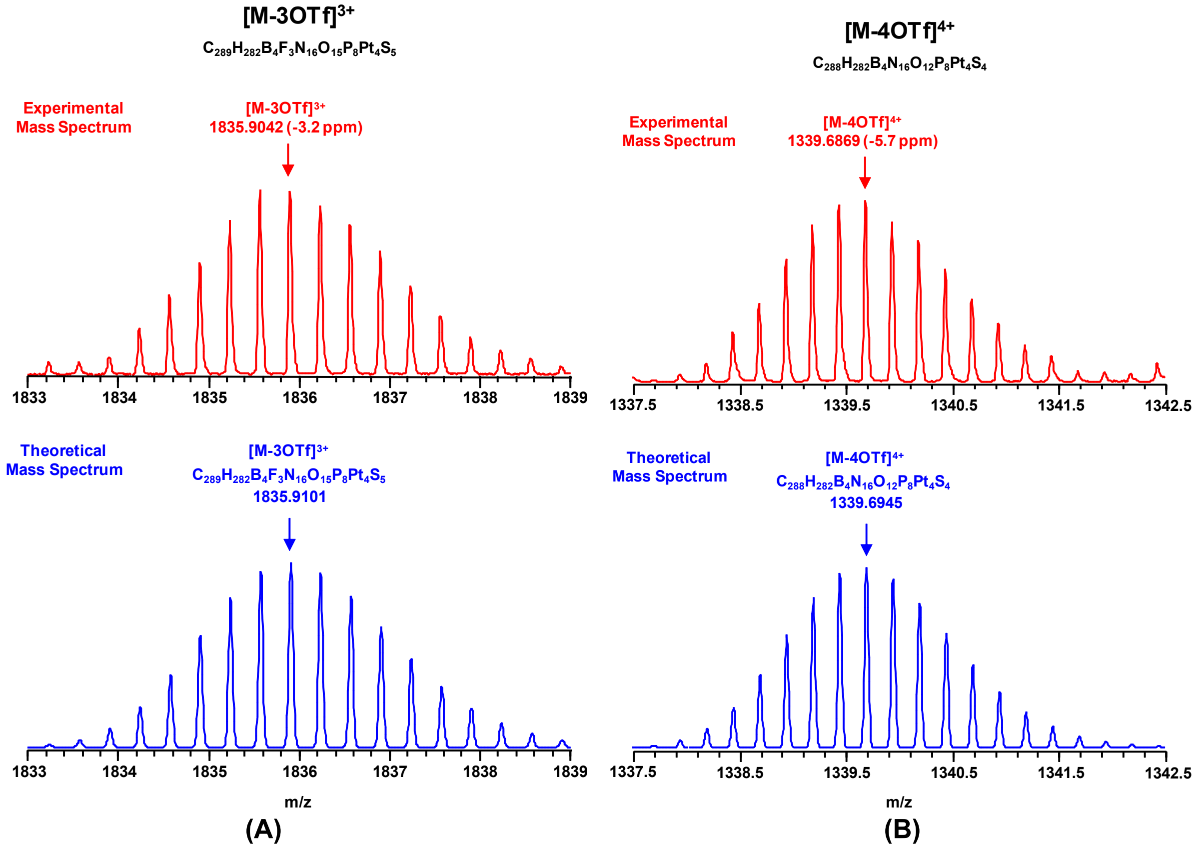


Figure S9. Experimental (red) and theoretical (blue) ESI mass spectra of **(A) [[(3)$_2$. 4SPy]**(OTf)**]$^{3+}$** and **(B)[(3)$_2$. 4SPy]$^{4+}$**.

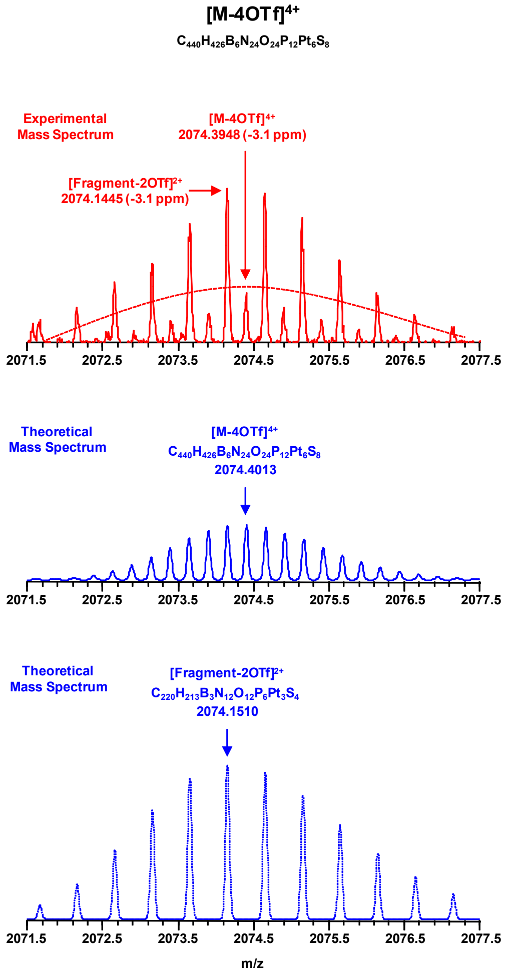
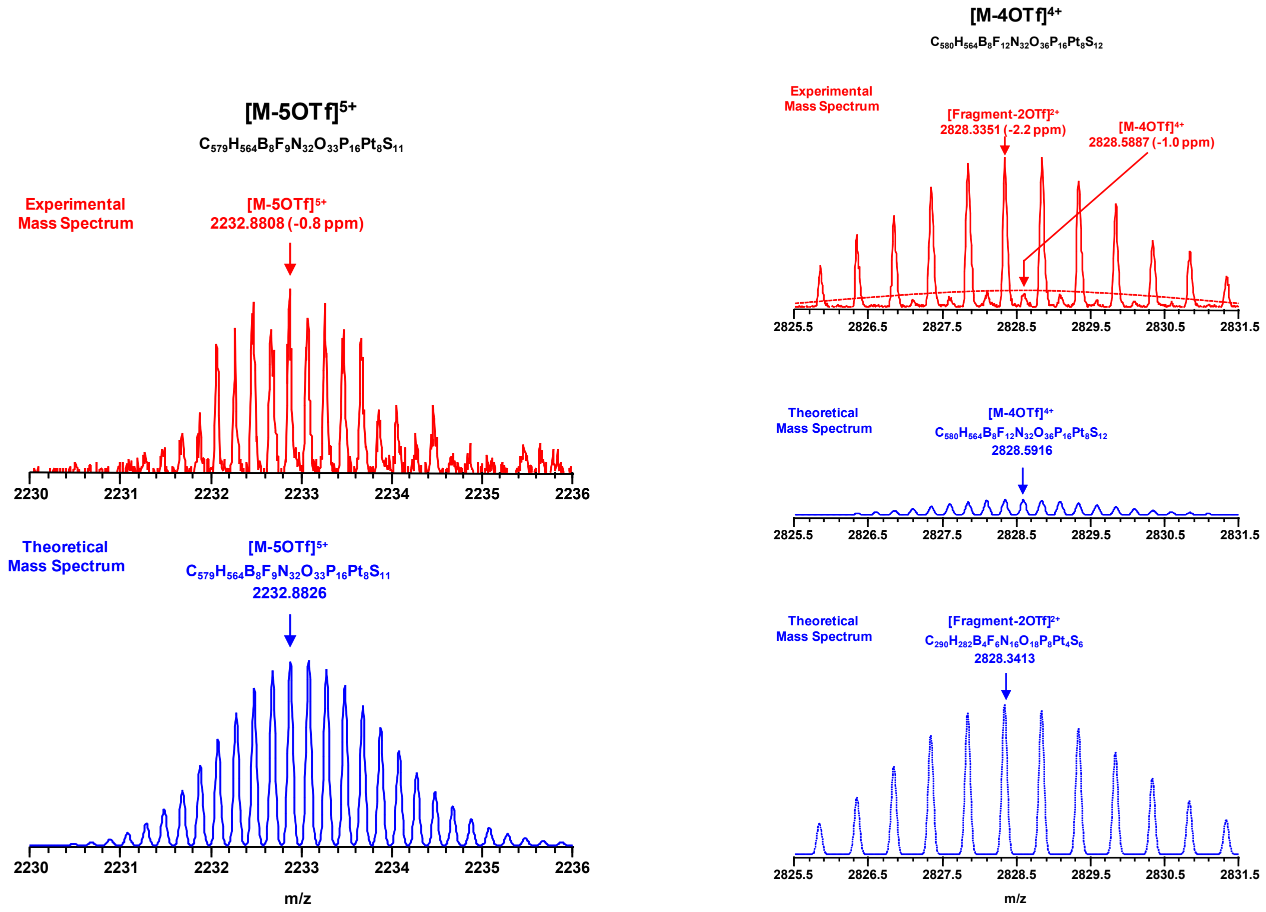


Figure S10. Experimental (red) and theoretical (blue) ESI mass spectra of **$[(3)_3 \cdot (4Spy)_2]^{4+}$**. The molecular ion of **$[(3)_3 \cdot (4Spy)_2]^{4+}$** is superimposed by the isotopic distribution of a doubly charged fragmentation product of the structure. The fragment is generated during the ESI process. The elemental composition of the fragment is $C_{220}H_{213}B_3N_{12}O_{12}P_6Pt_3S_4$ and its theoretical mass spectrum is displayed in the bottom (dashed blue).



(A) **(B)**

Figure S11. **(A)** Experimental (red) and theoretical (blue) ESI mass spectra of**[[(3)$_4$. (4Spy)$_2$]**(3OTf)**]**$^{5+}$. **(B)** Experimental (red) and theoretical (blue) ESI mass spectra of **[(3)$_4$. (4Spy)$_2$]**(4OTf)$^{4+}$. The molecular ion **[[(3)$_4$. (4Spy)$_2$]**(4OTf)**]**$^{4+}$ is superimposed by the isotopic distribution of a doubly charged fragmentation product of the structure. The fragment is generated during the ESI process. The elemental composition of the fragment is $C_{290}H_{282}B_4F_6N_{16}O_{18}P_8Pt_4S_6$ and its theoretical mass spectrum is displayed in the bottom (dashed blue)...

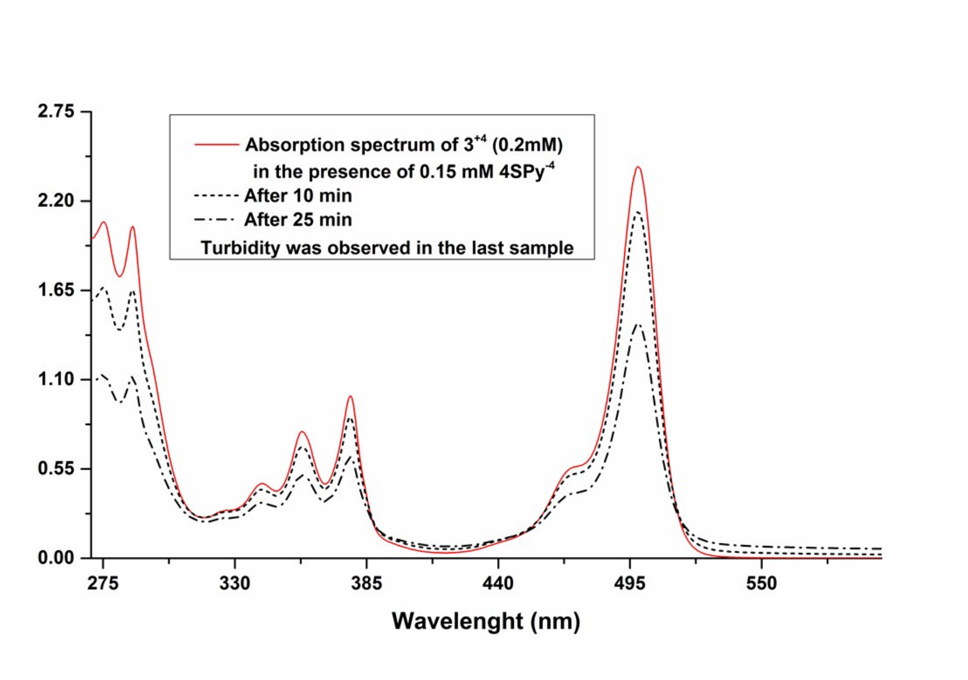


Figure S12. Time evolution of the absorption spectrum of the mixture consisting of **3**(OTf)$_4$ (0.2 mM) in the presence of **4Spy**(NBu$_4$)$_4$(0.15 mM).

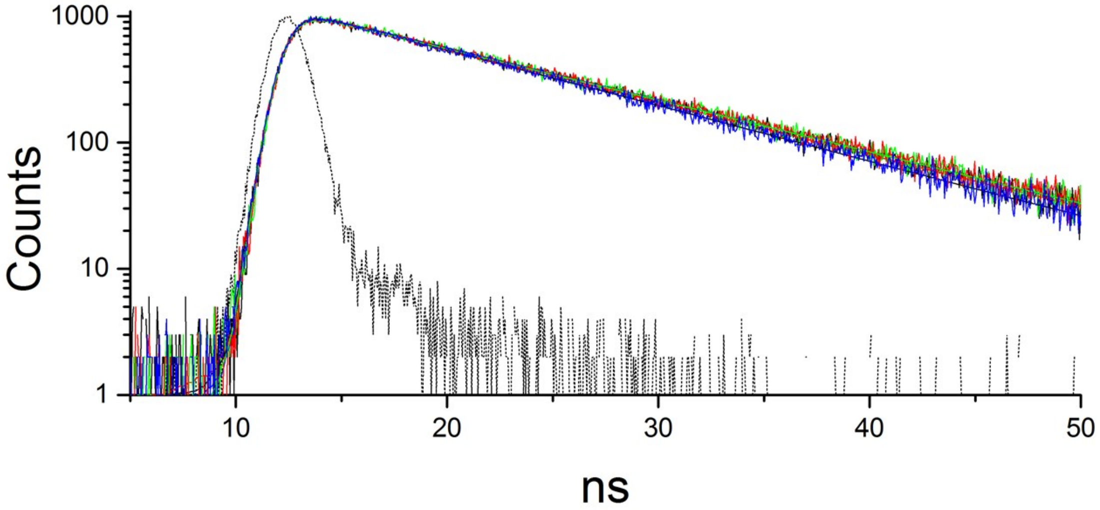


Figure S13. Fluorescence decay curves and fitting curves of **3^{+4}** vs the molar ratio R (em: at 525 nm, exc: at 358 nm) *black*: R = 0, τf = 10.1 ns; *green*: R = 0.13, τf = 10.3 ns; *red*: R = 0.26, τf = 10.4 ns; *blue*: R = 0.4, τf = 9.6 ns. Gray line is the pulse profile.

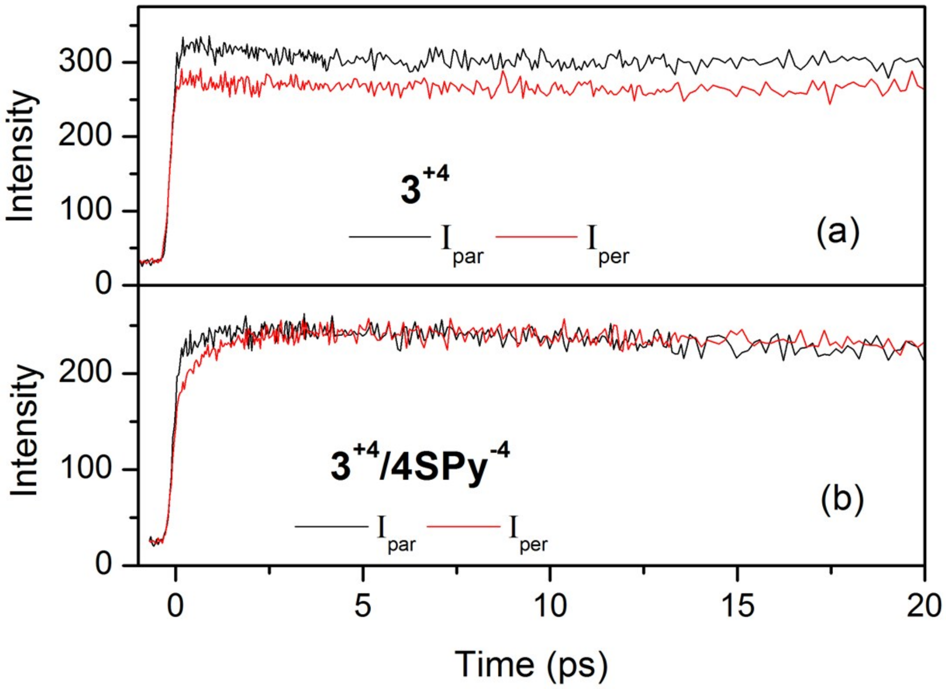


Figure S14. Fluorescence decays at 530 nm polarized parallel **(I_{par})** and perpendicularly **(I_{per})** to the excitation polarization plane after excitation at 380 nm for (a) **3^{+4}** alone and (b) in the presence of 0.4 equiv. of **$4Spy^{-4}$**.

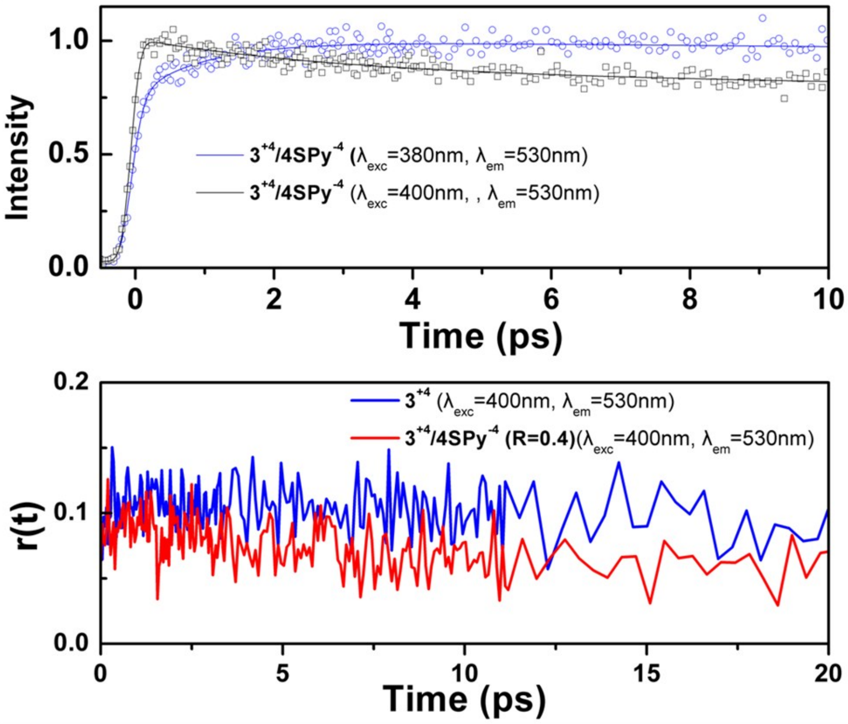


Figure S15.: Fluorescence decays (u*pper panel)* and anisotropies (*low panel*) at 530 nm of **3^{+4}** upon excitation at 400 nm in the absence (black) and the presence (blue) of 0.4 equiv. of **$4Spy^{-4}$**

X-ray Crystal Structure Determination

Single crystals suitable for analysis were grown by mixing 1.0 mL of **3**$^{+4}$ solution (0.2 mM) with 1 mL of **4SPy**$^{-4}$ (0.14 mM) and allowing the mixture undisturbed in a designator under reduced pressure at room temperature for 72 h. X-ray diffraction data were collected by the rotation method at 100 K using synchrotron radiation at the X06DA beamline (Swiss Light Source, Paul ScherrerInstitut, Villigen, Switzerland) on a crystal of dimensions 0.3x0.05x0.05 mm.

Crystal structure determination of the complex
Crystal data. (C268H248B4N12P8Pt4) x 0.5 • (C16H6O12S4) x 0.5 • (C15H15N5O5) x 0.5, M = 22319.90, orthorhombic, a = 31.680(6), b =38.340(7), c = 41.120(3) Å, V = 49944.8(6) Å**3, T = 100 K, space group Pccn (no.56), Z = 8, 86305 reflections measured, 19505 unique (Rint = 0.077) which were used in all calculations. The final R1 = 0.1252 for 11333 Fo>4sig(Fo) and 0.1828 for all data.

Structure solution & Refinement: Diffraction data up to 1.10 Å resolution were collected, which were processed and scaled with the XDS software[6]. The structure was solved by direct methods and refined by the program SHELXL97.[7]By alternating cycles of restrained full-matrix least-squares refinement and manual inspection the missing atoms of the host, as well as these of the guest and solvent molecules (11 molecules of DMF molecules at half occupancies) were found. Due to the presence of solvent molecules (more than the ones used in the refinement) and disorder, mainly of the numerous phenyl groups on the phosphorous atoms, the refinement of the structure was finished with many restraints on the bond distances of these phenyls, but also of the Bodipys. All atoms heavier than carbon atoms were refined by anisotropically and H-atoms were placed at idealized positions and refined by the riding model (UH = 1.20 or 1.25 UC). The solvent parameters were not refined at the end of the refinement.

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