

Supplementary Information

A palladium-hinged organometallic square with a perfect-sized cavity for the encapsulation of three heteroguests

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1.- General Comments

The preparation of the palladium-cornered metallo-square [3](BF₄)₄ was performed according to the literature method.¹ Anhydrous solvents were dried using the Solvent Purification System (SPS M BRAUN) or purchased and degassed prior to use. All other reagents were used as received from commercial suppliers. NMR spectra were recorded on a Varian Innova 500 MHz or on a Bruker 400/300MHz. NMR spectra were recorded at room temperature with CD₃CN as NMR solvent. All values of the chemical shift are in ppm regarding the δ -scale. Exact mass analysis were recorded by using a Q-TOF premier mass spectrometer with an electrospray source (Waters, Manchester, UK) operating at a resolution of about 16000 (FWHM).

1.1. ¹H NMR titration experiments.

The binding affinity of [3](BF₄)₄ with pyrene and triphenylene was studied by ¹H NMR titration experiments. The experiments were carried out in CD₃CN at constant concentration of Host (1 mM). The addition of the solution of the polyaromatic guest (from 0.5 to 50 equivalents) on the Host solution produced a perturbation on some of the Host proton resonances. All spectra recorded are given below. Association constants calculated by global nonlinear regression analysis.²

1.2. Uv-Vis. Titration experiments

The binding affinity of [3](BF₄)₄ towards coronene was studied by Uv-Vis. spectroscopy. The UV-Titrations experiments were carried out in CH₃CN at constant concentration of host (0.03 mM). The addition of the solution of coronene (from 0.2 to 10 equivalents) was monitored by Uv-Vis spectroscopy at 298K. All recorded spectra and data used for the determination of the association constants are given below. The association constant was calculated by global nonlinear regression analysis.²

1.3. Formation of Host:Hetero-Guests adducts.

The encapsulation of the different guests inside the Host's cavity was performed placing in an NMR tube a Host solution of 1 mM in CD₃CN and a suspension of the desired guests. Typically the process involved first the addition of two equivalents of the Polycyclic Aromatic Hydrocarbon (pyrene, triphenylene or coronene), and then two equivalents of NTCDI. The resulting suspensions were placed 30' in the ultrasonic bath before recording the spectra. The reverse addition of guests (first NTCDI and then PAH), afforded exactly the same final product.

2.- Encapsulation of guests G1-G4

2.1. Pyrene (G1)

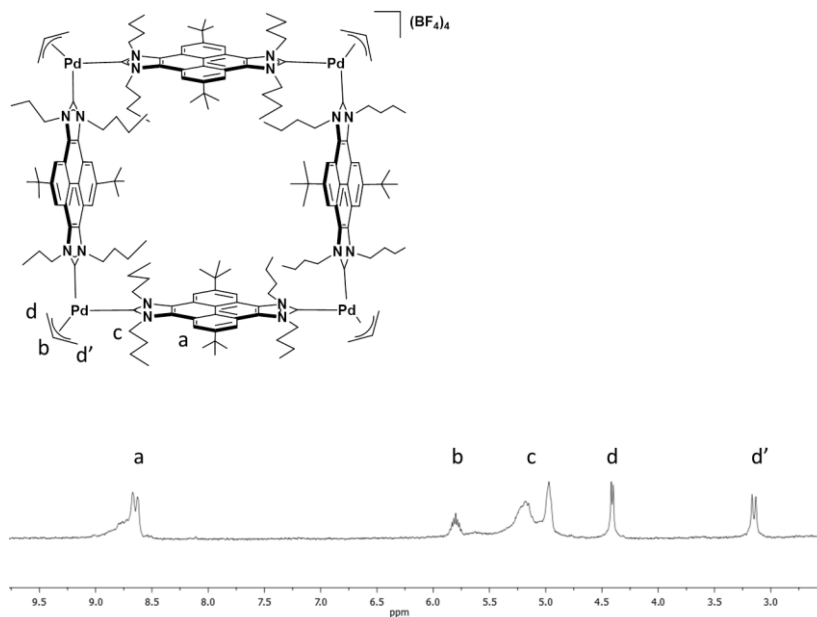


Figure S1. Selected region of ¹H NMR spectrum of [3](BF₄)₄ in CD₃CN at 298K

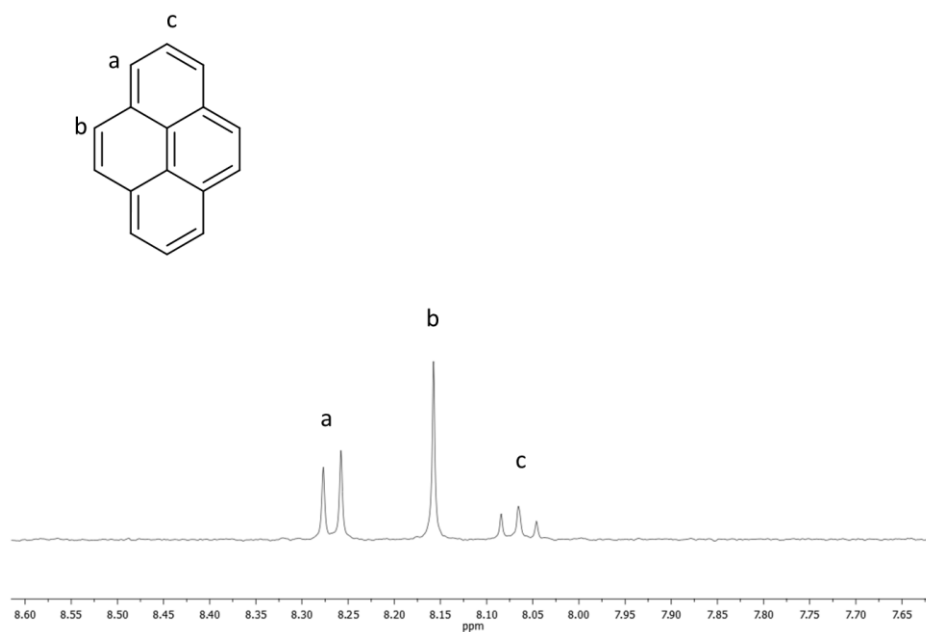


Figure S2. ¹H NMR spectrum of pyrene (G1) in CD₃CN at 298K

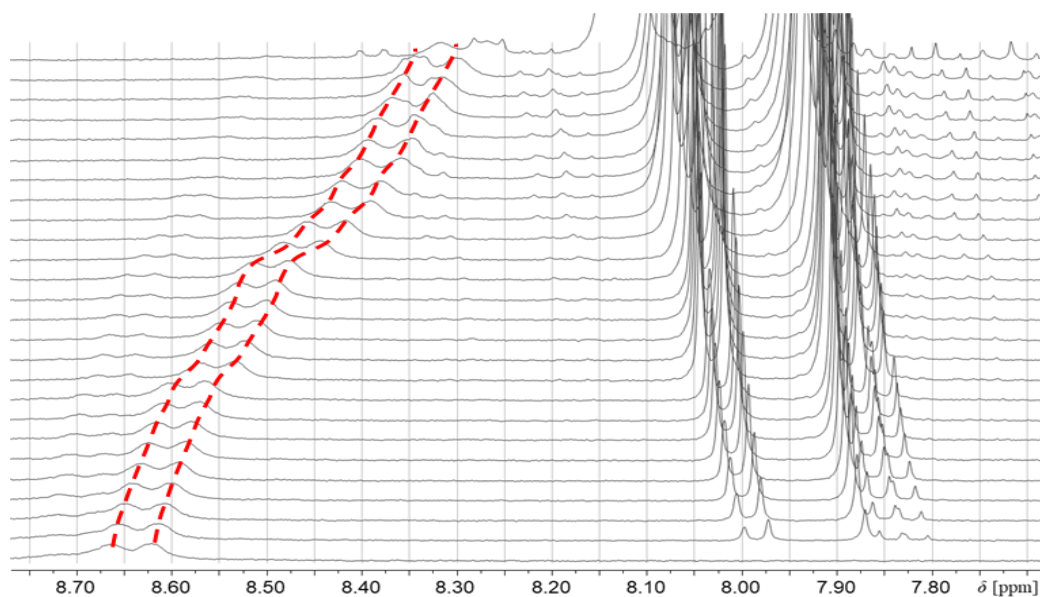


Figure S3. Selected region of ^1H NMR titration of $[\mathbf{3}](\text{BF}_4)_4$ with pyrene (G1) in CD_3CN at 298K

Table S1. Data values from the titration of $[\mathbf{3}](\text{BF}_4)_4$ with pyrene in CD_3CN at 298K

[H] (mM)	[G1] (mM)	Equiv. G1	δH (ppm)
1	0,00	0,00	8,64
1	0,25	0,25	8,64
1	0,50	0,50	8,63
1	0,74	0,74	8,62
1	0,98	0,98	8,61
1	1,36	1,36	8,6
1	1,74	1,74	8,59
1	2,11	2,11	8,59
1	2,47	2,47	8,58
1	3,70	3,70	8,55
1	4,55	4,55	8,54
1	5,36	5,36	8,53
1	6,14	6,14	8,52
1	6,90	6,90	8,51
1	8,33	8,33	8,49
1	10,00	10,00	8,46
1	11,54	11,54	8,44
1	14,29	14,29	8,41
1	16,67	16,67	8,4
1	18,75	18,75	8,39
1	22,22	22,22	8,38
1	25,00	25,00	8,37
1	27,27	27,27	8,36
1	50,00	50,00	8,29

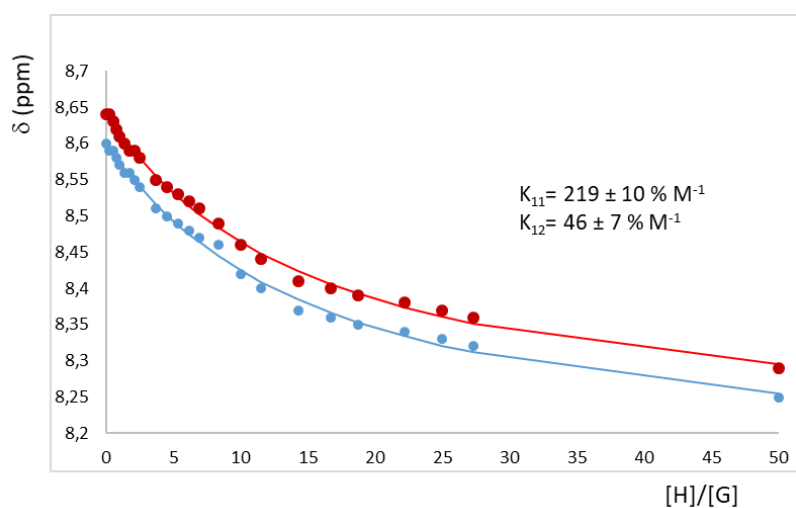


Figure S4. Binding isotherm and non-linear least-squares fitting of the chemical shift changes of H during titration experiments of $[3](BF_4)_4$ with pyrene (G1) in CD_3CN at 298K

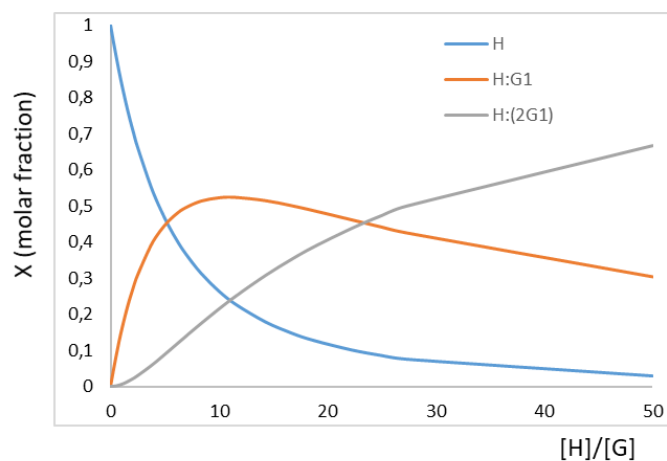


Figure S5. Speciation profiles of the titration of $[3](BF_4)_4$ with pyrene (G1) in CD_3CN at 298K

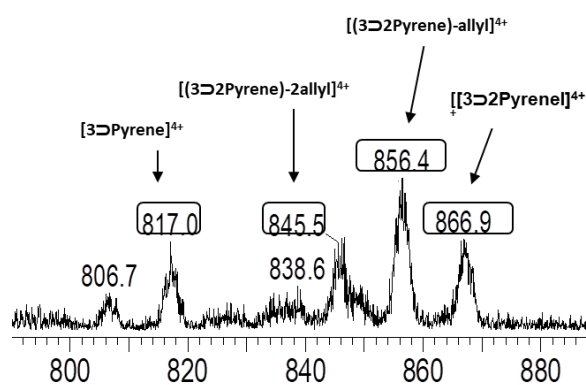


Figure S6. Selected region of HRMS spectrum of a mixture of $[3](BF_4)_4$ + pyrene in CH_3CN at 298K.

2.2. Triphenylene (G2)

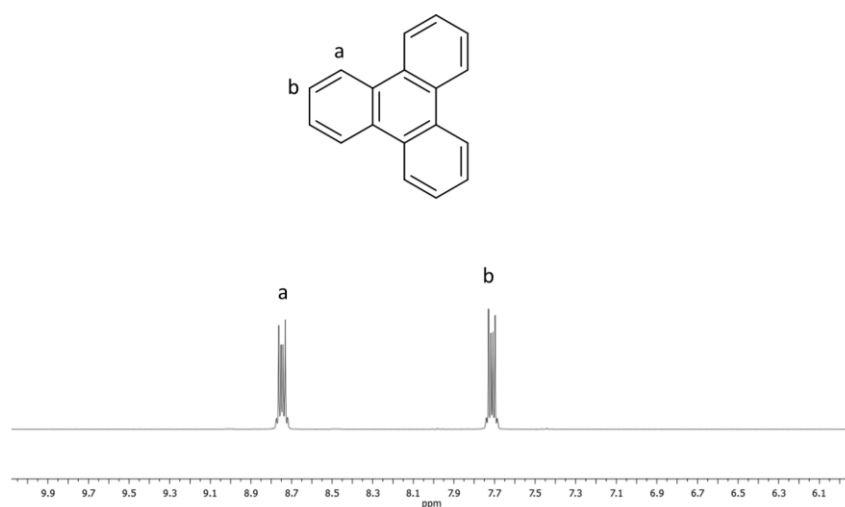


Figure S7. ^1H NMR Spectrum of triphenylene (G2) in CD_3CN at 298K

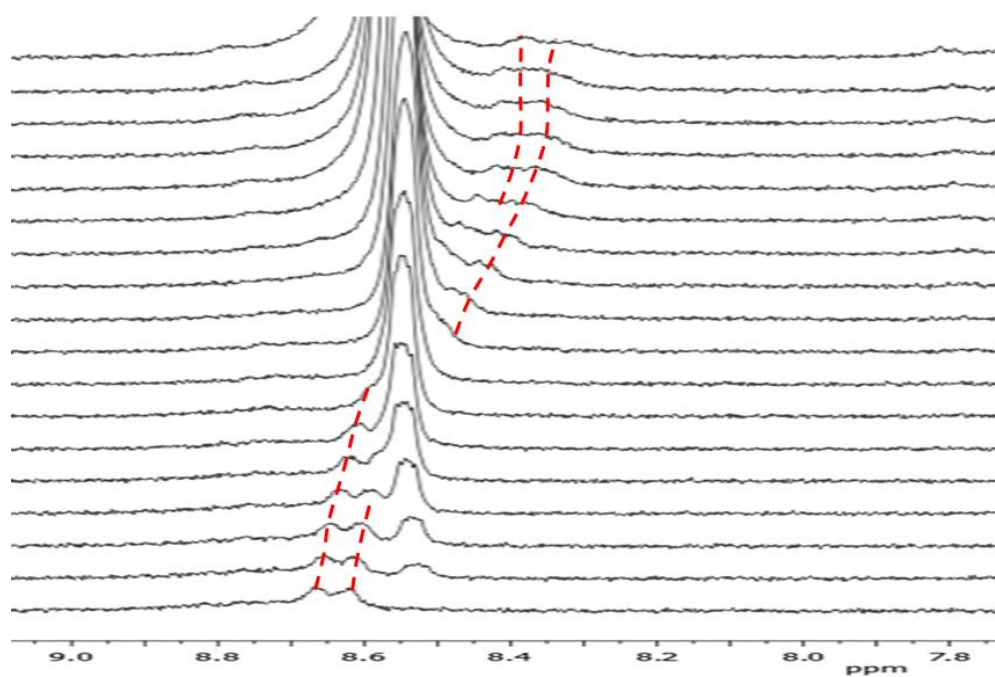


Figure S8. Selected region of ^1H NMR titration of $[\mathbf{3}](\text{BF}_4)_4$ with triphenylene (G2) in CD_3CN at 298K

Table S2. Data values from the titration of [3](BF₄)₄ with triphenylene (G2) in CD₃CN at 298K

[H] (mM)	[G2] (mM)	Equiv G2	δH (ppm)
0,5	0,00	0,00	8,64
0,5	0,20	0,40	8,64
0,5	0,39	0,78	8,64
0,5	0,58	1,17	8,64
0,5	0,77	1,54	8,63
0,5	0,95	1,90	8,63
0,5	1,13	2,26	8,63
0,5	1,31	2,62	8,62
0,5	1,48	2,96	8,62
0,5	1,65	3,30	8,62
0,5	1,82	3,64	8,61
0,5	2,14	4,29	8,61
0,5	2,46	4,91	8,60
0,5	2,76	5,52	8,60
0,5	3,33	6,67	8,59
0,5	3,87	7,74	8,59
0,5	5,07	10,15	8,57
0,5	6,11	12,22	8,56
0,5	7,01	14,03	8,54
0,5	8,51	17,01	8,52
0,5	9,69	19,38	8,51
0,5	11,45	22,91	8,48
0,5	20,00	40,00	8,39

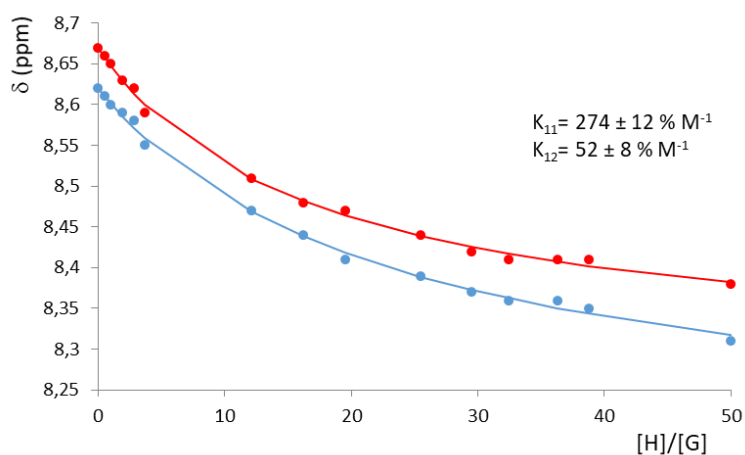


Figure S9. Binding isotherm and non-linear least-squares fitting of the chemical shift changes of H during titration experiments of [3](BF₄)₄ with triphenylene (G2) in CD₃CN at 298K

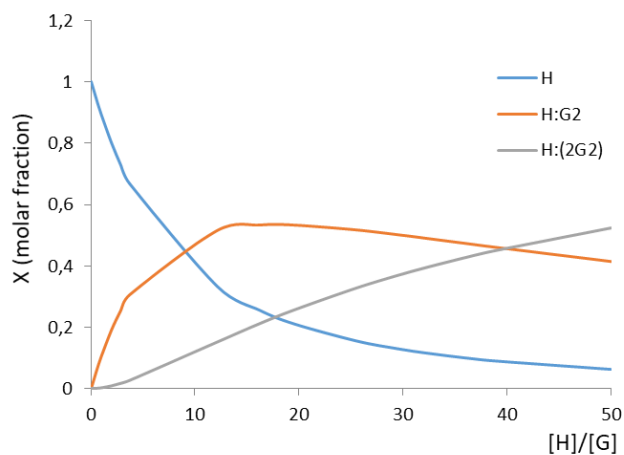


Figure S10. Speciation profiles of the titration of $[3](BF_4)_4$ with triphenylene (G2) in CD_3CN at 298K.

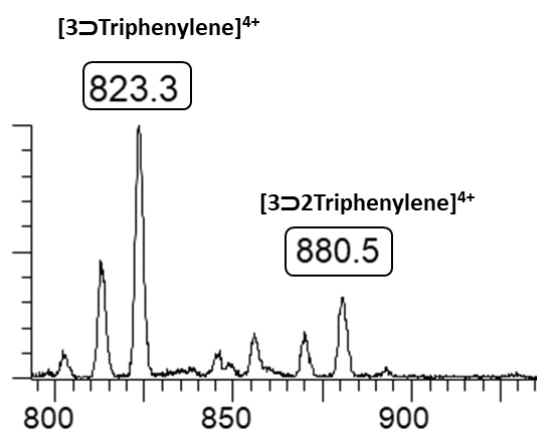


Figure S11 Selected region of HRMS spectrum of a mixture of $[3](BF_4)_4$ + triphenylene in CH_3CN at 298K. The peaks directly below 823.3 and 880.5 belong to the loss of the allyl fragment being $[(3\text{-triphenylene})\text{-allyl}]^{4+}$ and $[(3\text{-2triphenylene})\text{-allyl}]^{4+}$ as indicated for the Pyrene analogue (G1).

2.3. *N,N'*Dimethyl Naphtalene Tetracarboxylic Diimide, NTCDI (G3)

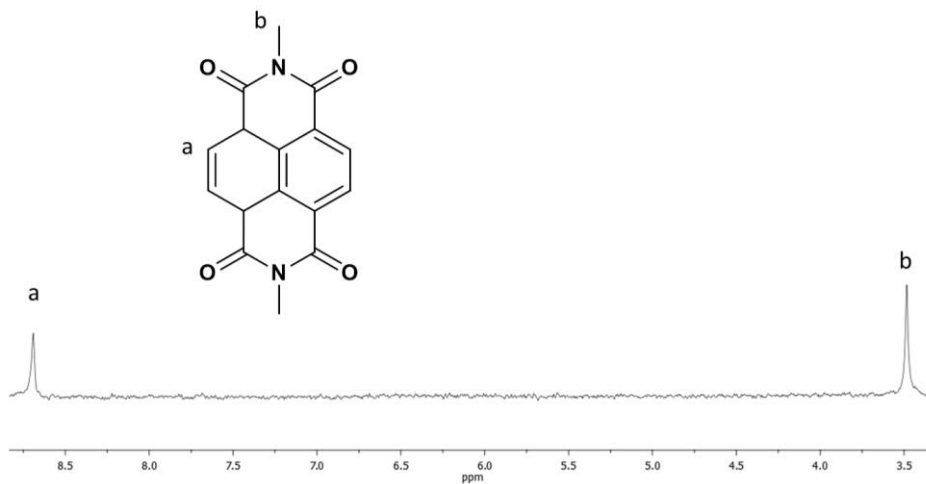


Figure S12. Selected region of ¹H NMR Spectrum of NTCDI (G3) in CD₃CN at 298K

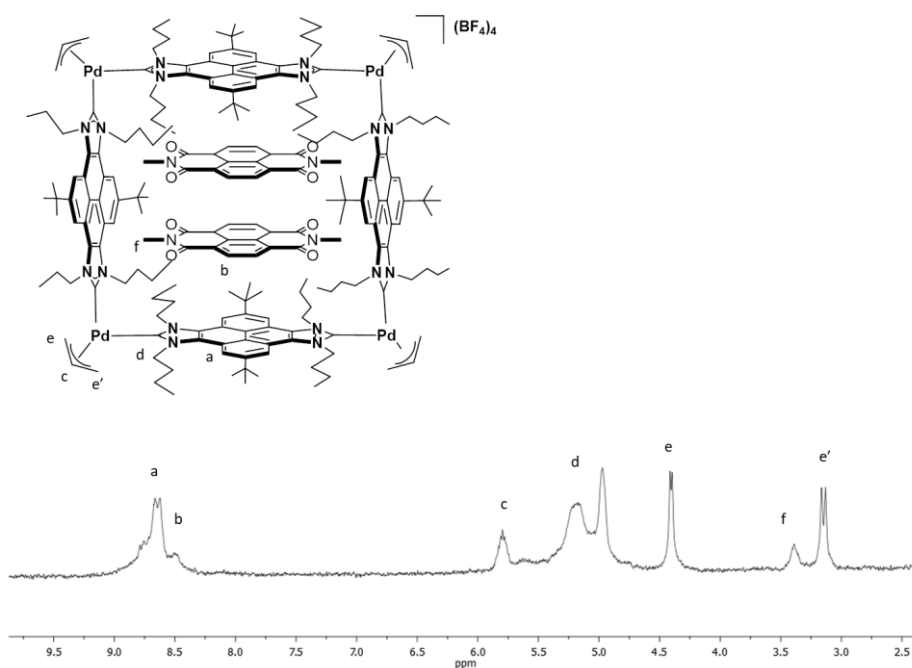


Figure S13. Selected region of ¹H NMR spectrum of a mixture of [3](BF₄)₄ + NTCDI (3 eq.)

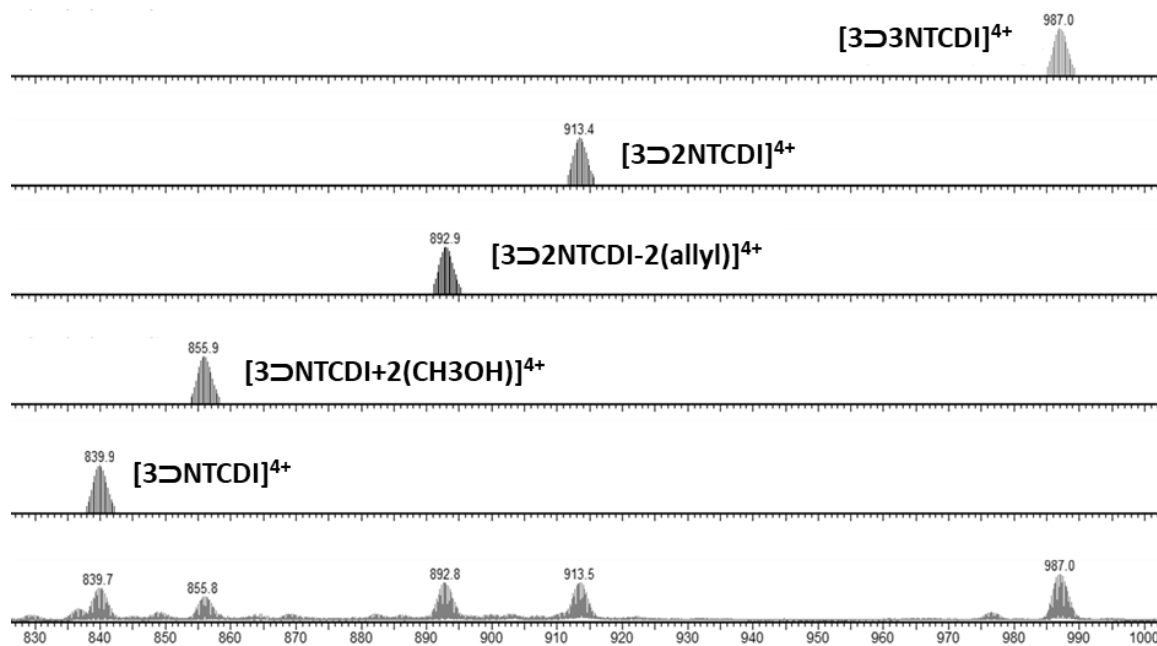


Figure S14. Selected region of HRMS spectrum of a mixture of of $[3](BF_4)_4 + NTCDI$ in CD_3CN at 298K. Bottom spectrum belongs to the sample with NTCDI (G3) and $[3]^{4+}$ while simulated spectra of $3\text{D}NTCDI$, $3\text{D}2NTCDI$ and $3\text{D}3NTCDI$ are added (together with $(3\text{D}NTCDI + 2CH_3OH)$ and $(3\text{D}2NTCDI - 2allyl)$).

2.4 Coronene (G4)

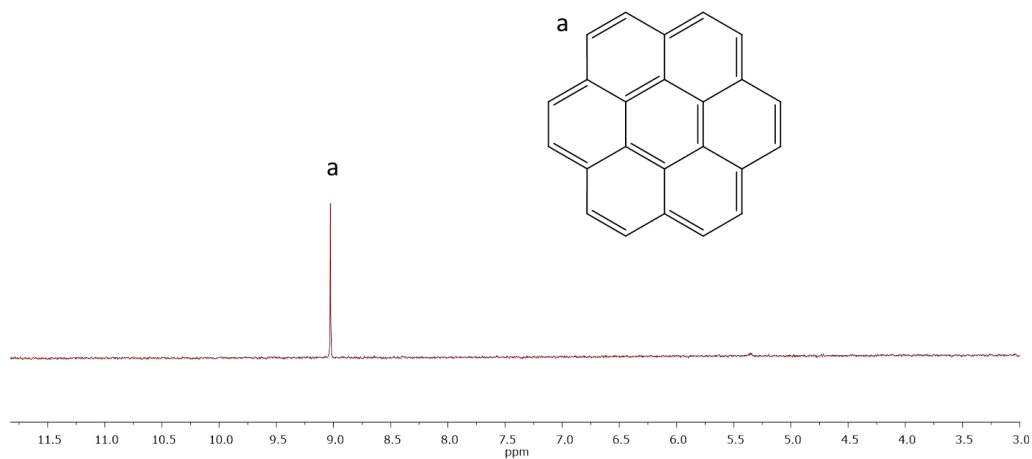


Figure S15. ^1H NMR spectrum of coronene (G4) in CD_3CN at 298K

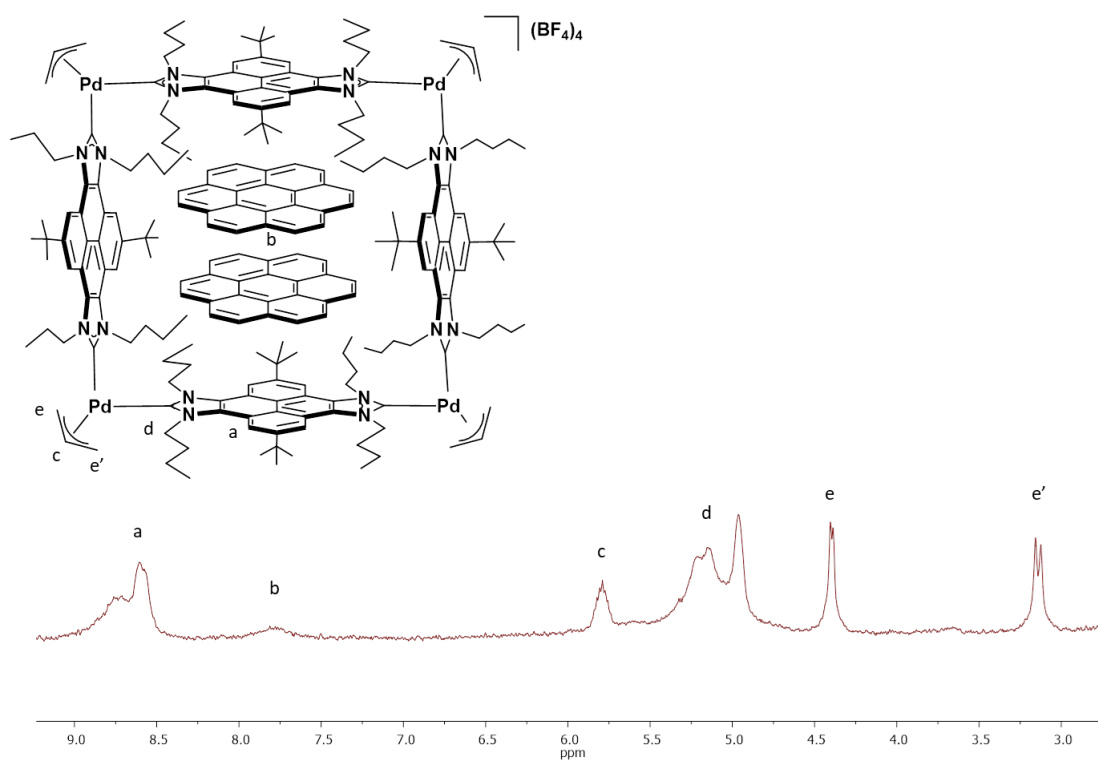


Figure S16. Selected region of the ^1H NMR spectrum of a mixture of $[\mathbf{3}](\text{BF}_4)_4$ + coronene (3 eq.) in CD_3CN at 298K

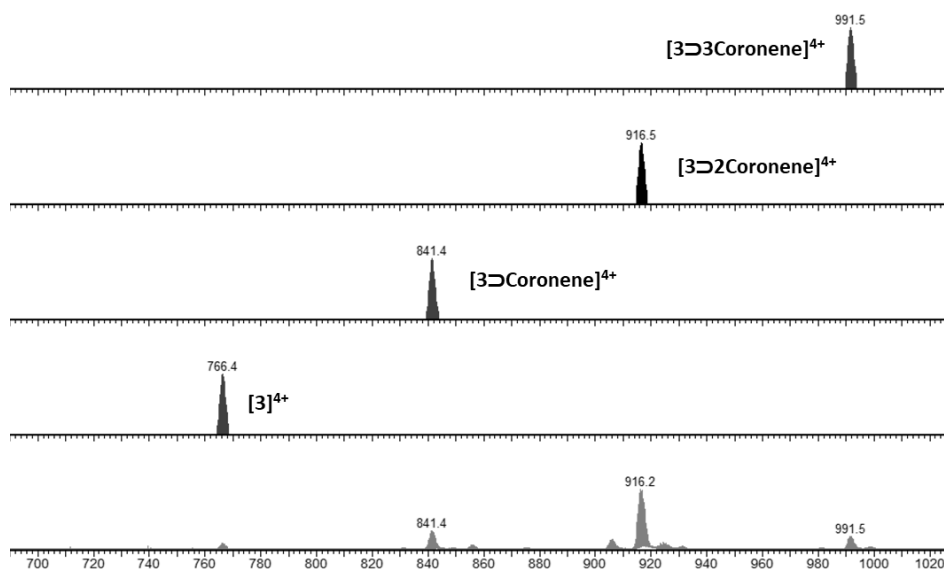


Figure S17. Selected region of HRMS spectrum of a mixture of $[3](BF_4)_4$ + coronene in CD_3CN at 298K. Bottom spectrum belongs to a solution of $[3](BF_4)_4$ and coronene. Simulated spectra of $[3]^{4+}$, $[3\text{-}coronene]^{4+}$, $[3\text{-}2coronene]^{4+}$ and $[3\text{-}3coronene]^{4+}$ are 2nd, 3rd, 4th and 5th from bottom to top.

Table S3. Data values from the titration of $[3](BF_4)_4$ with coronene (G4) in CH_3CN at 298K

[H] mM	[G] mM	Equiv.	Abs ($\lambda=323$ nm)	Abs ($\lambda=334$ nm)	Abs ($\lambda=339$ nm)	Abs ($\lambda=345$ nm)
0,030	0,000	0,000	1,329	1,837	2,180	1,917
0,030	0,007	0,244	1,437	1,926	2,416	1,968
0,030	0,015	0,499	1,559	2,001	2,685	2,029
0,030	0,023	0,762	1,661	2,075	2,845	2,069
0,030	0,030	1,011	1,755	2,143	3,002	2,113
0,030	0,037	1,247	1,840	2,208	3,174	2,162
0,030	0,045	1,489	1,922	2,255	3,243	2,188
0,030	0,052	1,736	2,052	2,363	3,391	2,250
0,030	0,060	2,000	2,126	2,413	3,442	2,270
0,030	0,067	2,248	2,192	2,463	3,610	2,306
0,030	0,074	2,481	2,239	2,478	3,406	2,311
0,030	0,090	2,995	2,339	2,576	3,763	2,372
0,030	0,105	3,496	2,421	2,592	3,641	2,374
0,030	0,120	3,994	2,548	2,719	3,807	2,462
0,030	0,150	4,987	2,653	2,794	3,818	2,494
0,030	0,180	5,992	2,780	2,911	3,936	2,594
0,030	0,210	7,010	2,911	3,010	3,775	2,628
0,030	0,240	7,998	2,999	3,083	3,809	2,693
0,030	0,270	8,999	3,135	3,191	4,135	2,760
0,030	0,300	10,000	3,234	3,237	3,980	2,784

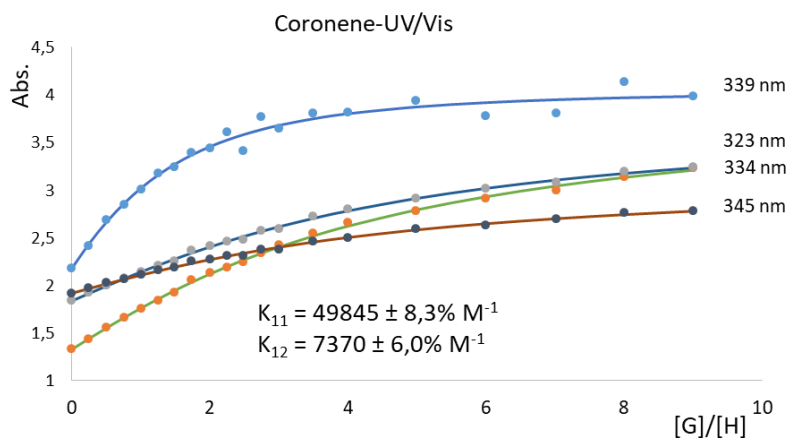


Figure S18. Binding isotherm and non-linear least-squares fitting of the absorption changes during titration experiments of $[\mathbf{3}](\text{BF}_4)_4$ with Coronene (G4) at a constant $[\text{H}] = 0.03 \text{ mM}$, in CH_3CN 298K.

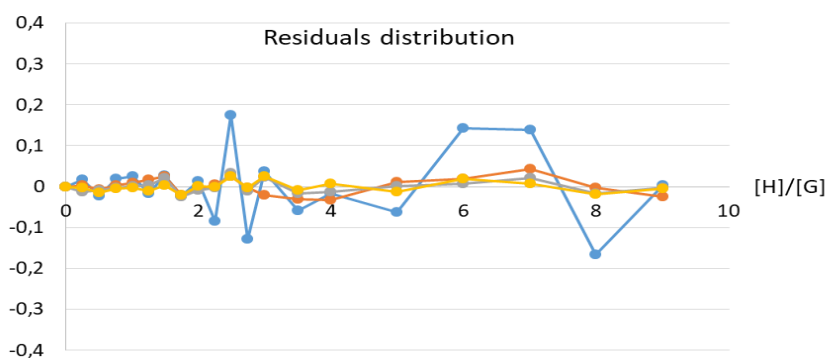


Figure S19. Residuals distribution of the UV titration of $[\mathbf{3}](\text{BF}_4)_4$ with coronene (G4).

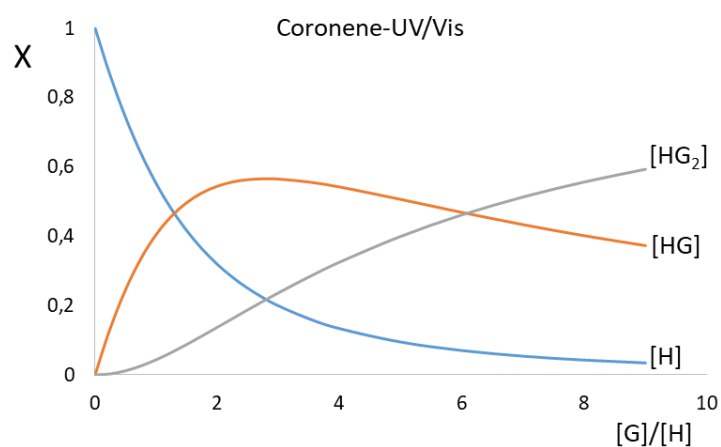


Figure S20. Speciation profiles of the UV titration of $[\mathbf{3}](\text{BF}_4)_4$ with coronene G4 at a $[\text{H}] = 0.03 \text{ mM}$ in CH_3CN 298K.

3.- Formation of Host:Hetero-Guests adducts

3.1. [3⊃(pyrene+2NTCDI)]⁴⁺

i) ¹H NMR Spectrum of Pyrene (G1)+ NTCDI (G3)

In order to confirm that the perturbations in the chemical shift observed not only in the host but also in the guest protons are due to the encapsulation process ¹H NMR Spectrum of the Guests G1+G3 without [3](BF₄)₄ was performed.

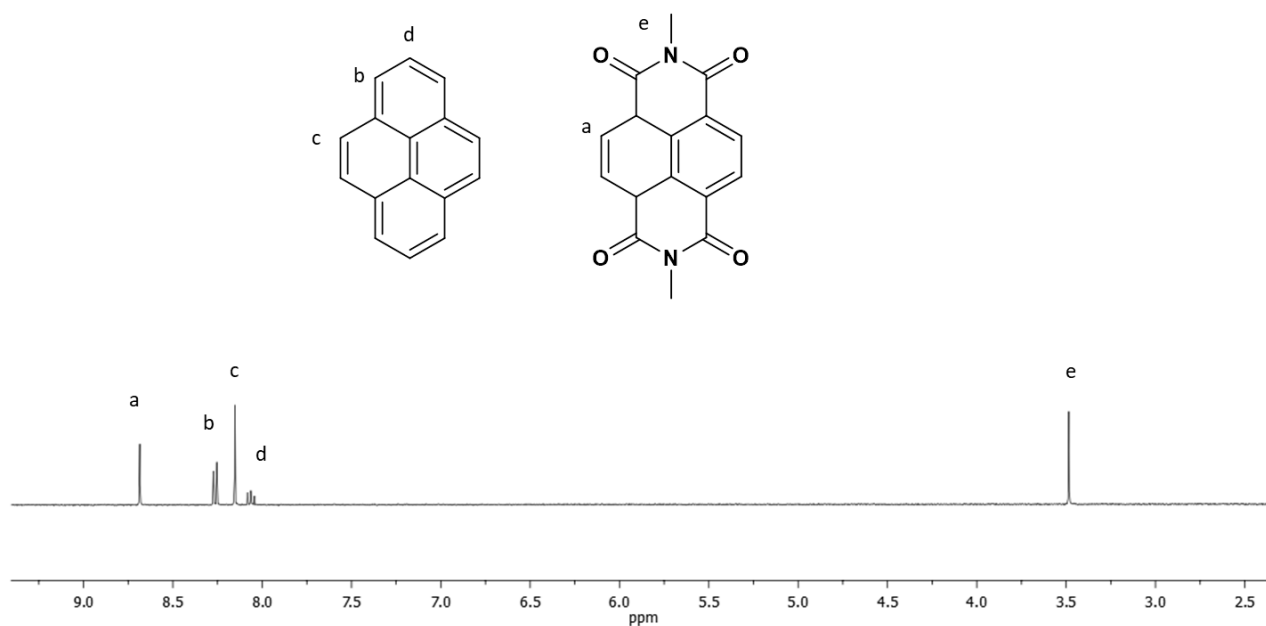


Figure S21. ¹H NMR spectrum of pyrene (G1) and NTCDI (G3) in CD₃CN at 298K

ii) Sequential Encapsulation of G1 and G3

The encapsulation of the different guests inside the Host's cavity was performed placing in an NMR tube a solution of host (1 mM) in CD₃CN, and a suspension of the desired guest. First G1, then G3. After the addition of the guest, the suspension was placed 30' in the ultrasonic bath before recording the spectra.

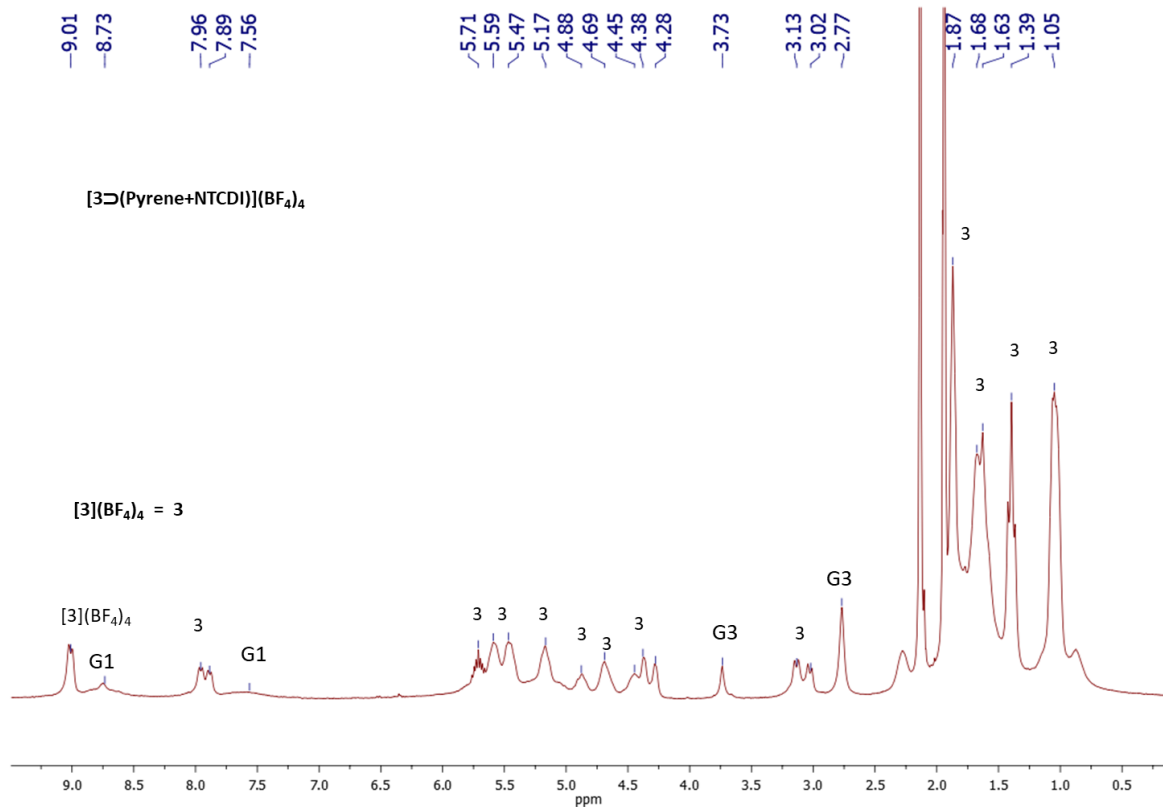


Figure S22. Selected region of the ^1H NMR spectrum of $[\mathbf{3}-(\text{Pyrene}+2\text{NTCDI})]^{4+}$ in CD_3CN at 298K

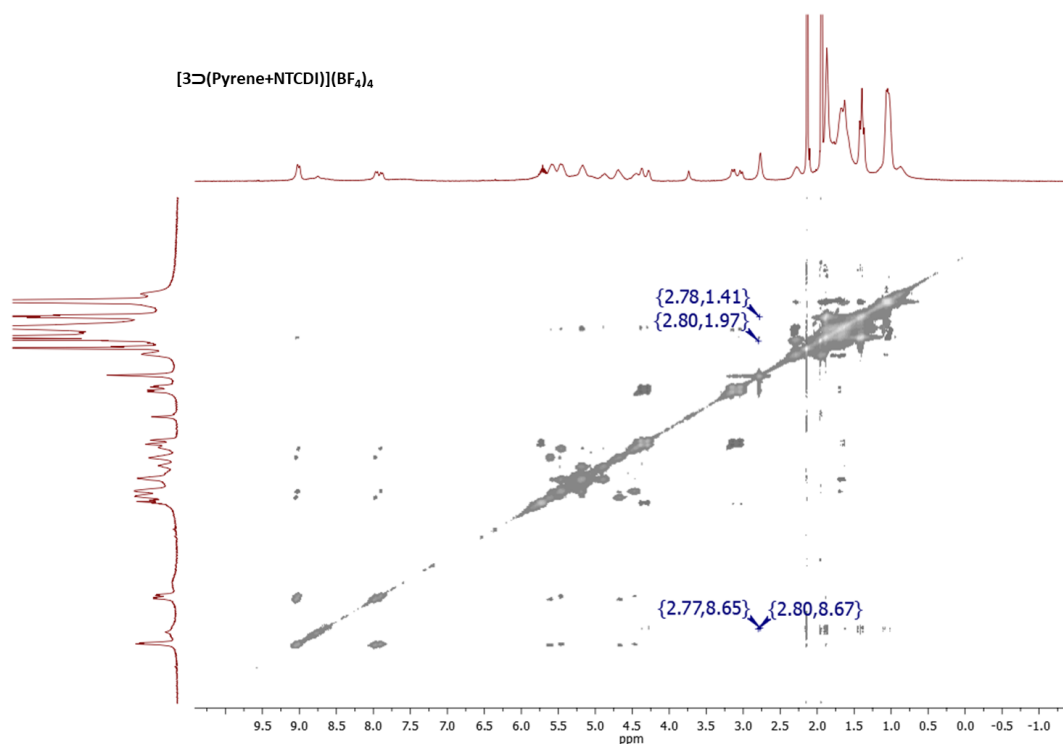


Figure S23. Full ROESY NMR spectrum of $[\mathbf{3}-(\text{Pyrene}+2\text{NTCDI})]^{4+}$ in CD_3CN at 298K

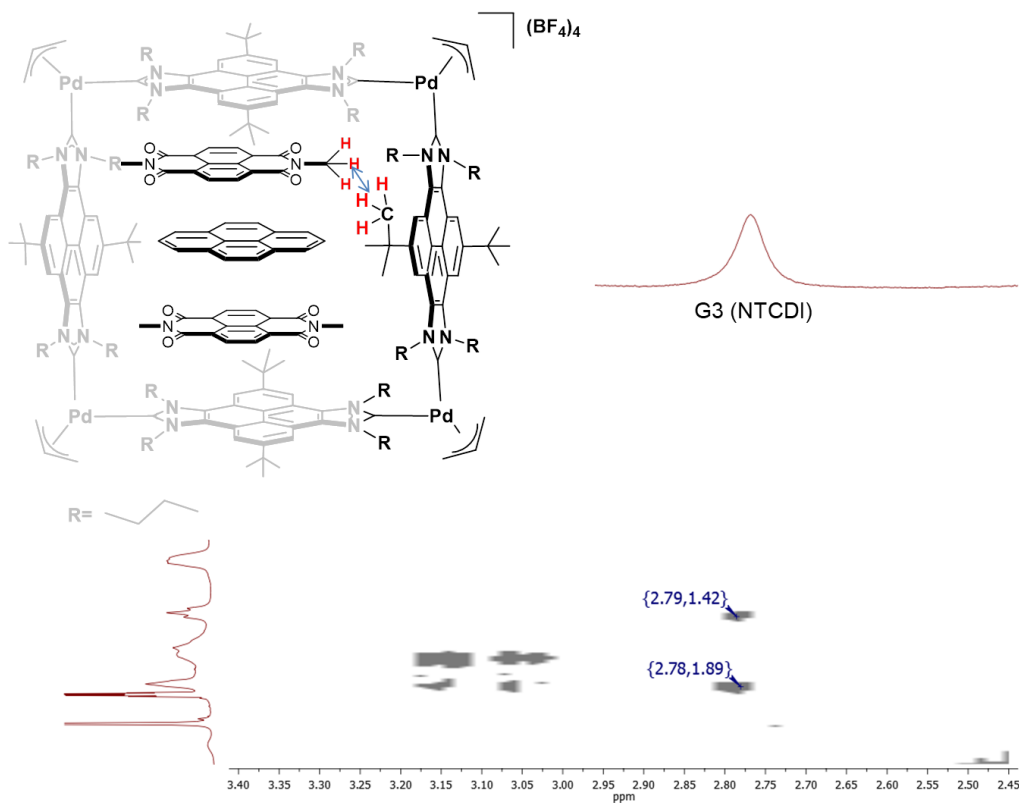


Figure S24. Selected region of ROESY NMR spectrum of $[3-(\text{Pyrene}+2\text{NTCDI})]^{4+}$ in CD_3CN at 298K

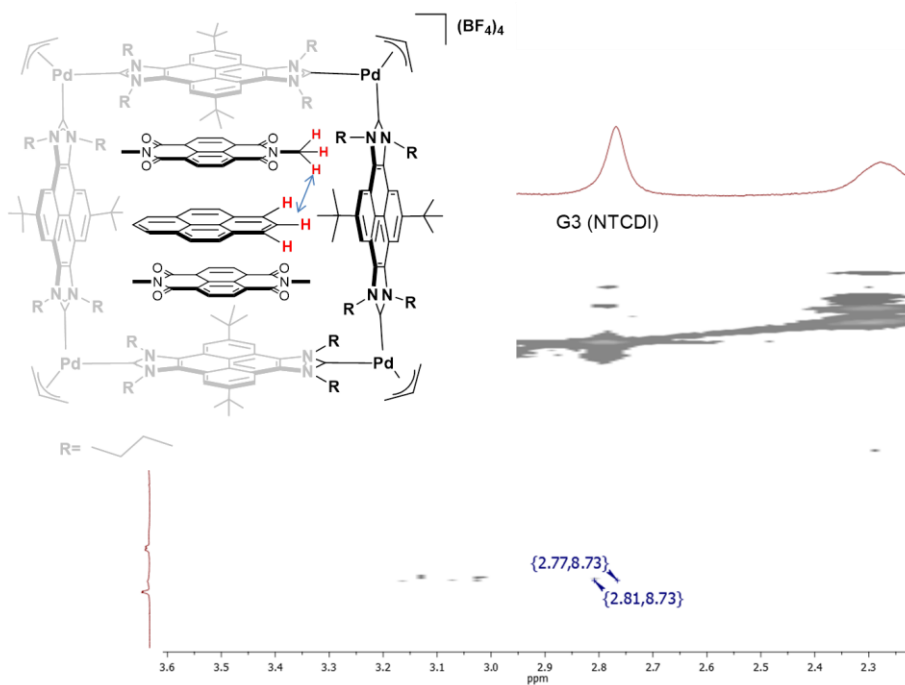


Figure S25. Selected region of ROESY NMR spectrum of $[3-(\text{Pyrene}+2\text{NTCDI})]^{4+}$ in CD_3CN at 298K

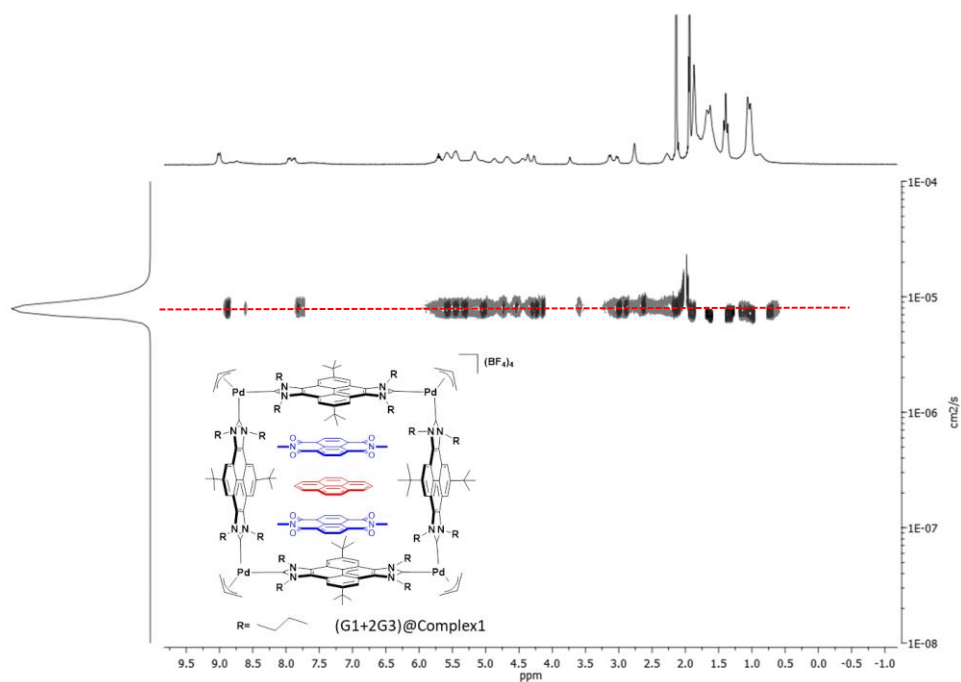


Figure S26. Selected region of DOSY NMR Spectrum of $[3\text{⊃}(\text{Pyrene}+2\text{NTCDI})]^{4+}$ in CD_3CN at 298K. Diffusion Coefficient = $7.78 \cdot 10^{-6} \text{ (cm}^2/\text{s)} = 7.78 \cdot 10^{-10} \text{ (m}^2/\text{s)}$.

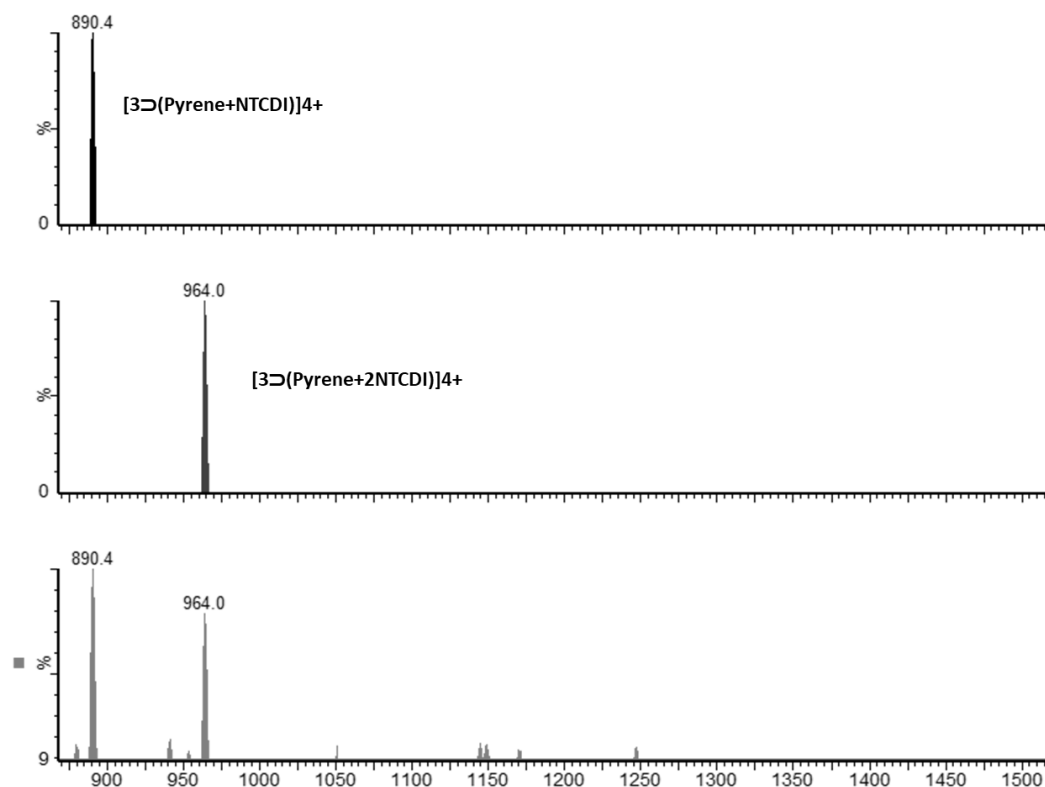


Figure S27. Selected region of HRMS spectrum of $[3\text{⊃}(\text{pyrene}+2\text{NTCDI})]^{4+}$ in CH_3CN at 298K. The first spectrum is the simulation of $[3\text{⊃}(\text{pyrene}+\text{NTCDI})]^{4+}$; the second spectrum is simulation of $[3\text{⊃}(\text{pyrene}+2\text{NTCDI})]^{4+}$ and the third spectrum is the sample in which both species are observed.

3.2. [3⊃(triphenylene+2NTCDI)]⁴⁺

i) NMR Spectrum of triphenylene (G2)+ NTCDI (G3)

In order to confirm that the perturbations in the chemical shift observed not only in the host but also in the guest protons are due to the encapsulation process ¹H NMR Spectrum of the Guests G2+G3 without [3](BF₄)₄ was performed.

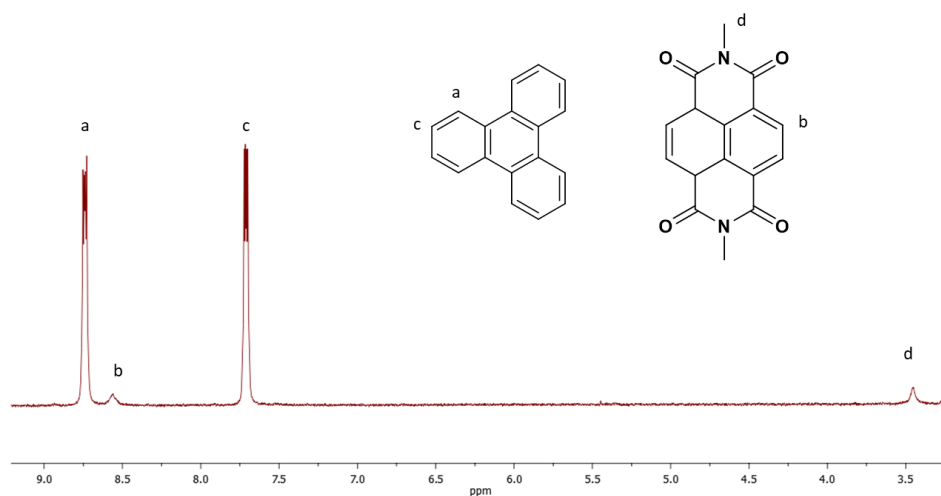


Figure S28. ¹H NMR Spectrum of triphenylene (G2) and NTCDI (G3) in CD₃CN at 298K

ii) Sequential Encapsulation of G2 and G3 inside [3](BF₄)₄

The encapsulation of the different Guest inside the Host's cavity was performed placing in an NMR tube a Host solution of 1 mM in CD₃CN and a suspension of the desired Guest. First G2, then G3. After the addition of the Guest, the suspension was placed 30' in the ultrasonic bath before recording the spectra.

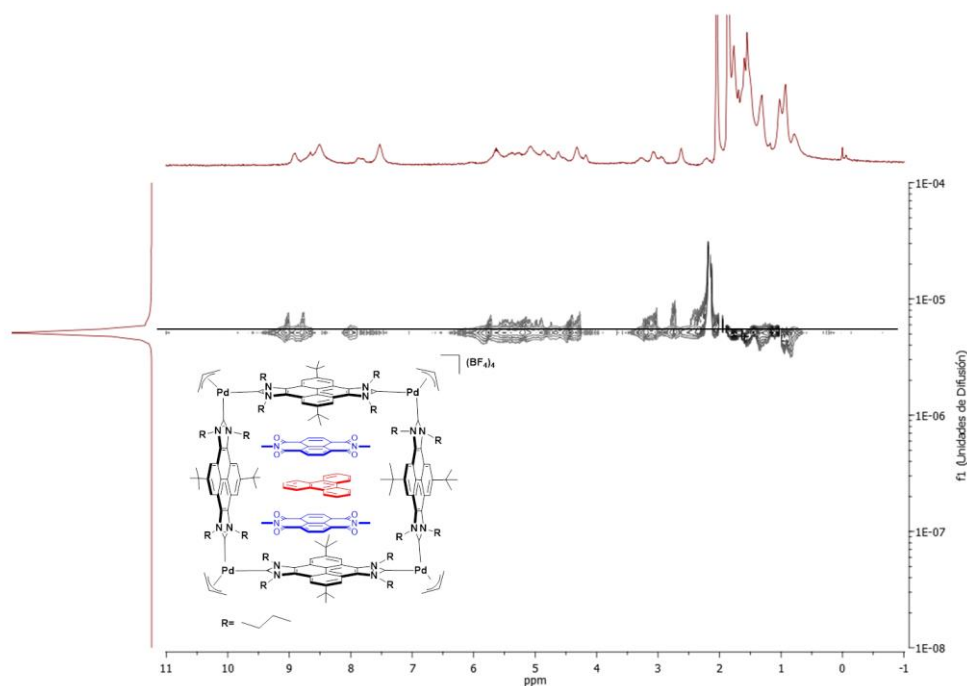


Figure S29. Selected region of DOSY NMR spectrum of $[3\text{D}(\text{triphenylene}+2\text{NTCDI})]^{4+}$ in CD_3CN at 298K. Diffusion Coefficient = $5.09 \cdot 10^{-6} \text{ (cm}^2/\text{s)} = 5.09 \cdot 10^{-10} \text{ (m}^2/\text{s)}$

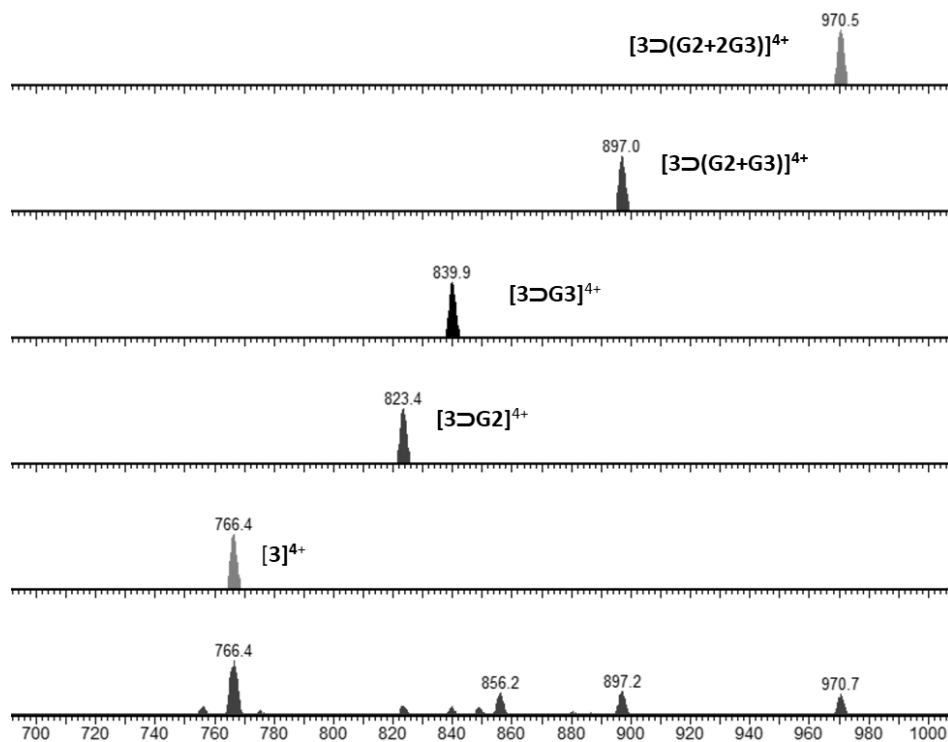


Figure S30. Selected region of HRMS spectrum of $[3\text{D}(\text{Pyrene}+2\text{NTCDI})]^{4+}$ in CH_3CN at 298K. Bottom spectrum belongs to experimental spectrum. Simulated spectra of $[3]^{4+}$, $[3\text{D}(\text{Triphenylene})]^{4+}$, $[3\text{D}(\text{NTCDI})]^{4+}$ and $[3\text{D}(\text{Triphenylene}+\text{NTCDI})]^{4+}$ are 2nd, 3rd, 4th and 5th from bottom to top.

3.3. [3⊃(coronene+2NTCDI)]⁴⁺

i) NMR spectrum of coronene (G4) + NTCDI (G3)

In order to confirm that the perturbations in the chemical shift observed not only in the host but but also in the guest protons are due to the encapsulation process ¹H NMR Spectrum of the Guests G3+G4 without [3](BF₄)₄ was performed

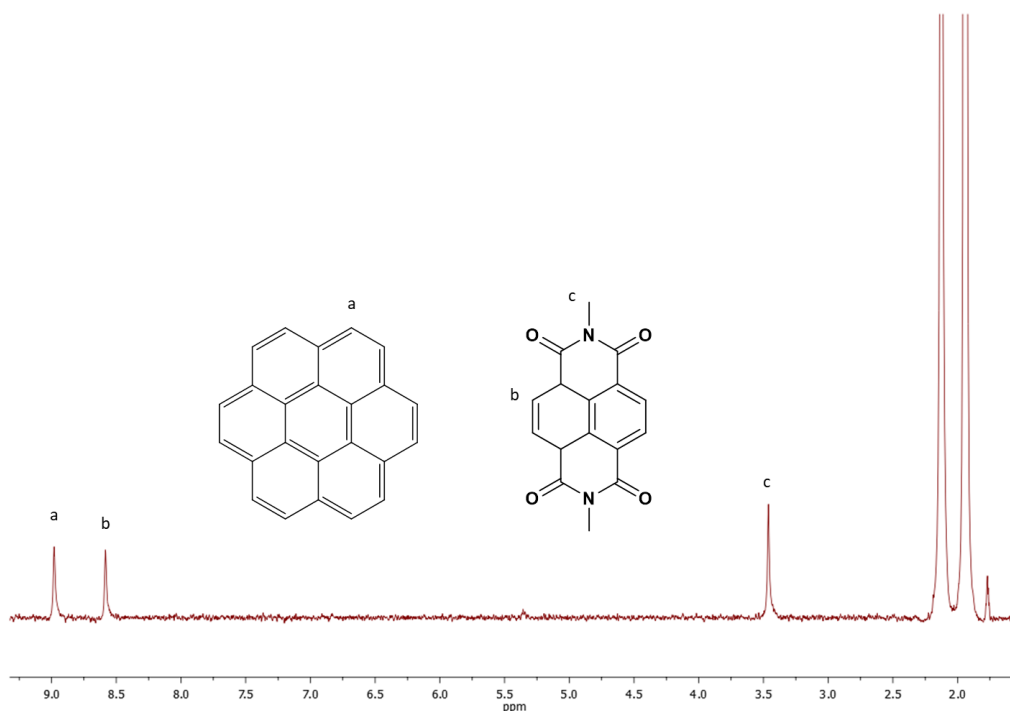


Figure S31. ¹H NMR spectrum of coronene (G4) and NTCDI (G3) in CD₃CN at 298K

ii) Sequential Encapsulation of G4 and G3 inside [3](BF₄)₄

The encapsulation of the different Guest inside the Host's cavity was performed placing in an NMR tube a Host solution of 1 mM in CD₃CN and a suspension of the desired Guest. First G4, then G3. After the addition of the Guest, the suspension was placed 30' in the ultrasonic bath before recording the spectra.

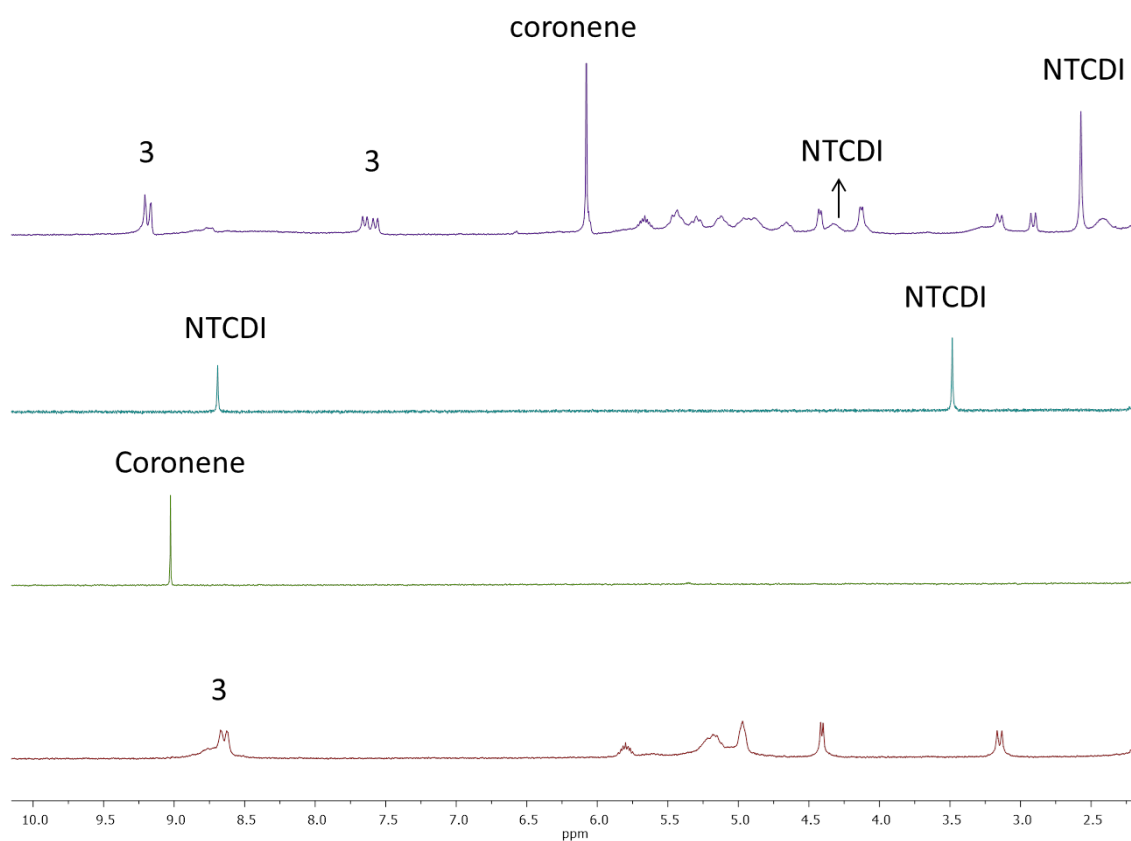


Figure S32. From bottom to top, ^1H NMR spectra of $[\mathbf{3}](\text{BF}_4)_4$, G4 (coronene), G3 (NTCDI) and $[\mathbf{3}\supset(\text{coronene}+2\text{NTCDI})]^{4+}$.

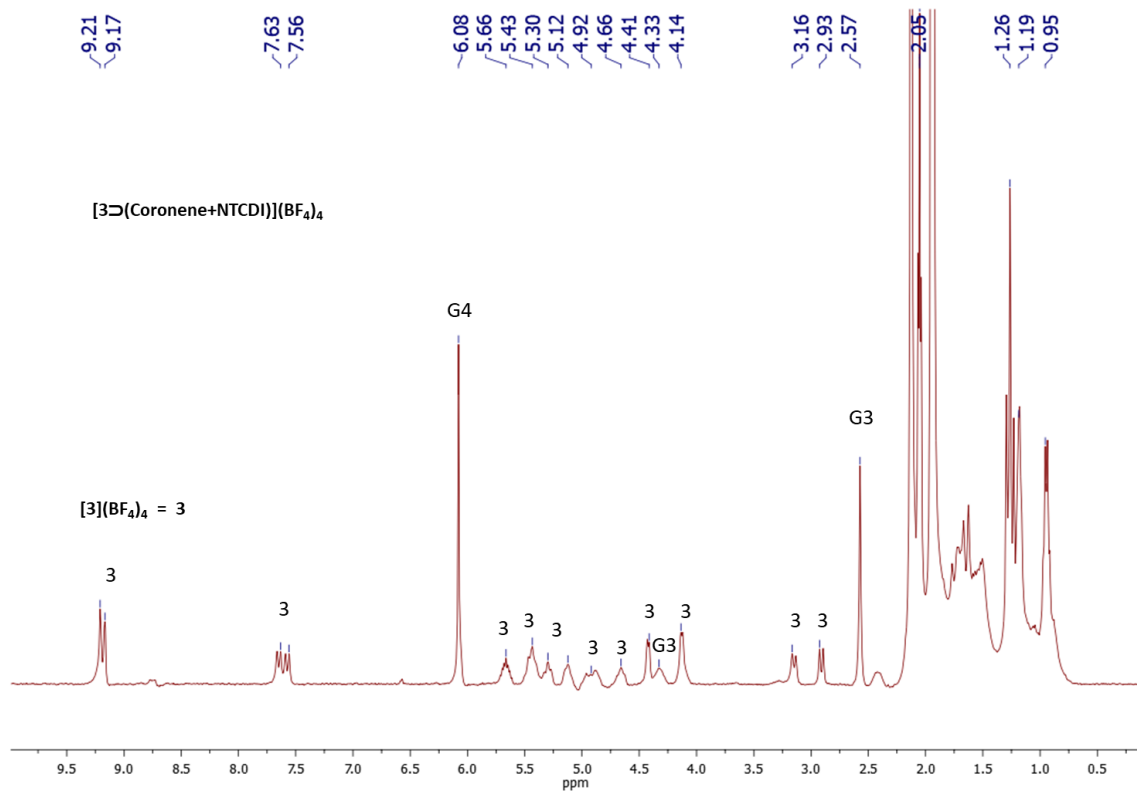


Figure S33. ^1H NMR spectrum of $[3\text{-(coronene+2NTCDI)}]^{4+}$ in CD_3CN at 298K

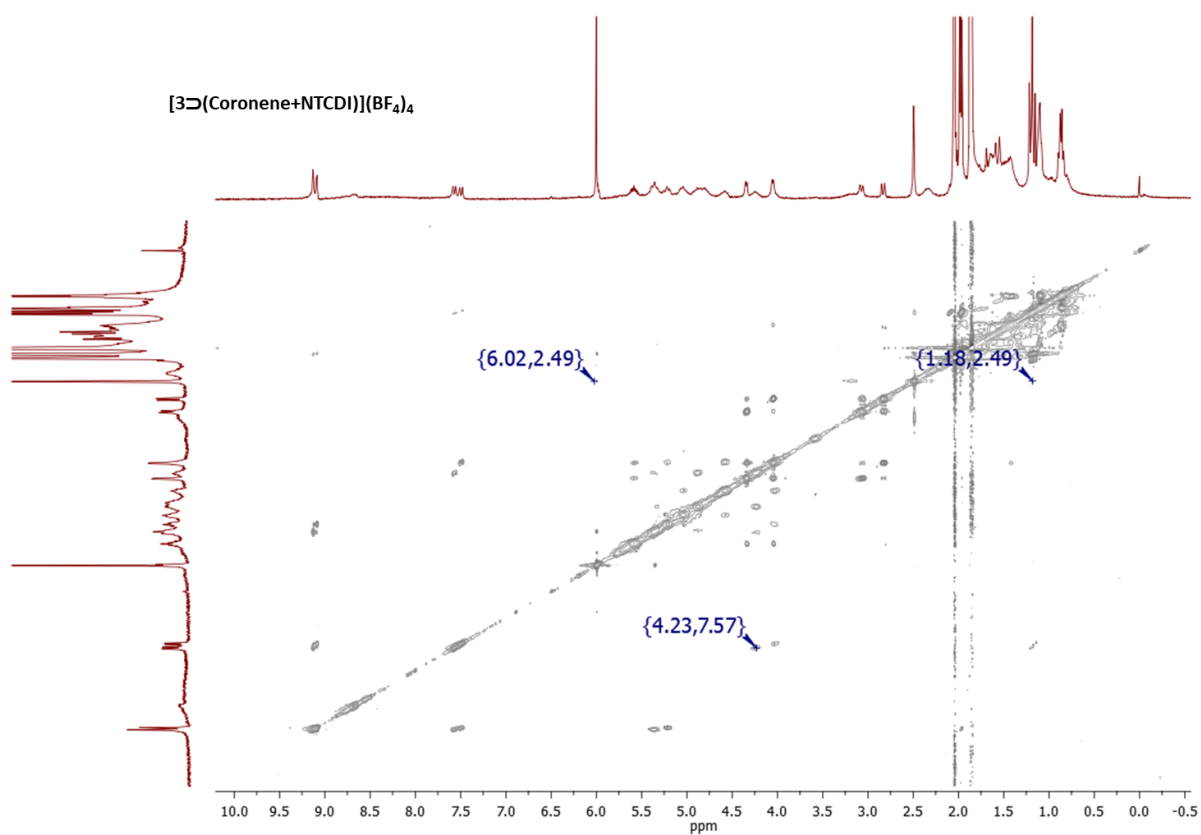


Figure S34. Full ROESY NMR spectrum of $[3\text{-(coronene+2NTCDI)}]^{4+}$ in CD_3CN at 298K

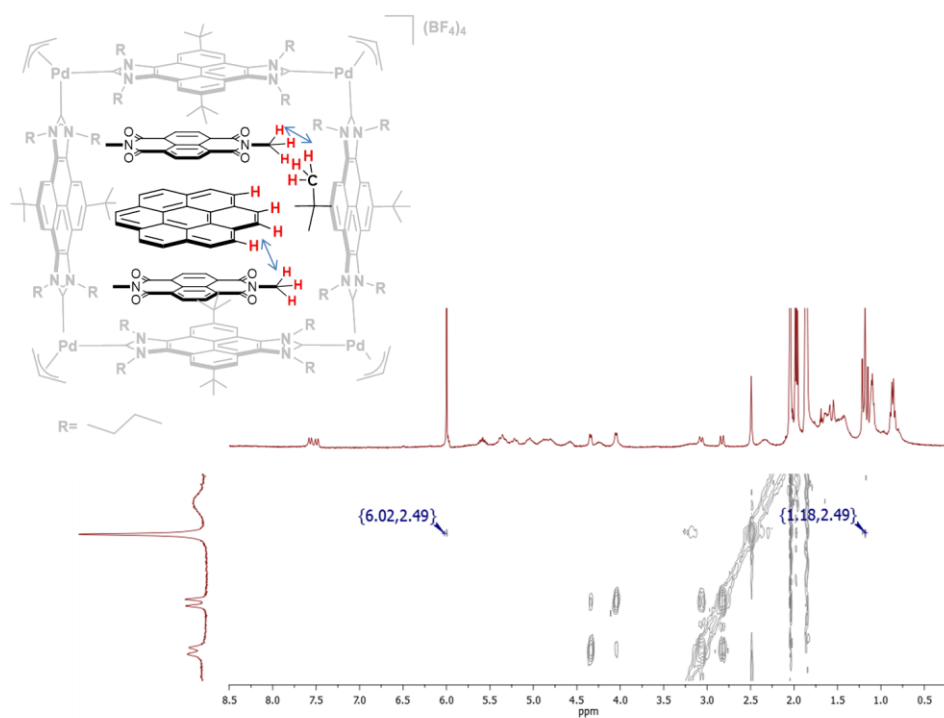


Figure S35. Selected area of the ROESY NMR of $[3\supset(\text{coronene}+2\text{NTCDI})]^{4+}$ in CD_3CN at 298K

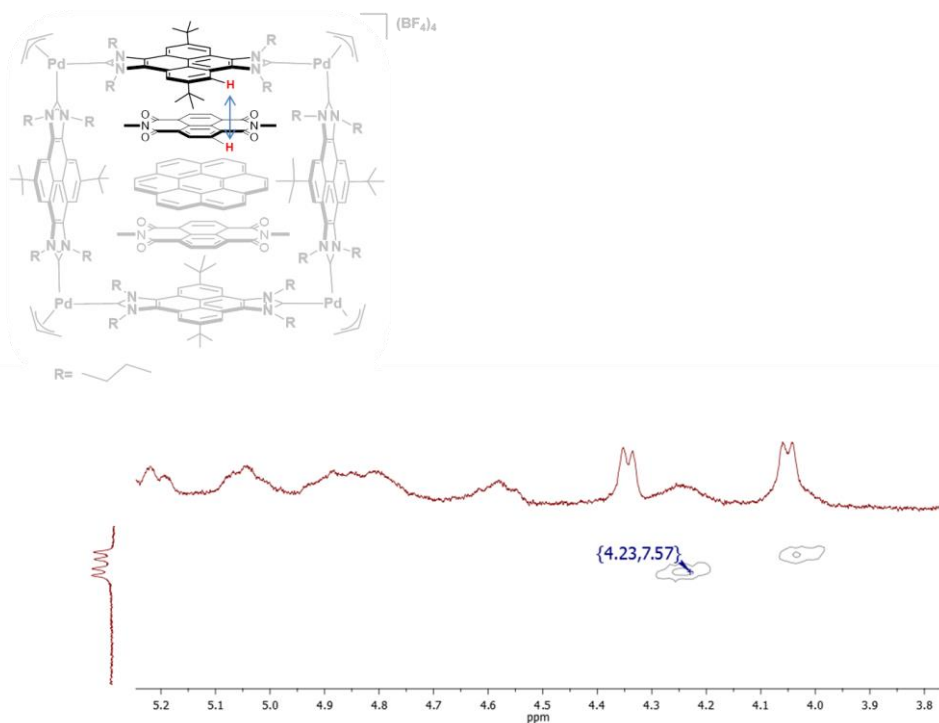


Figure S36. Selected area of the ROESY NMR spectrum of $[3\supset(\text{coronene}+2\text{NTCDI})]^{4+}$ in CD_3CN at 298K

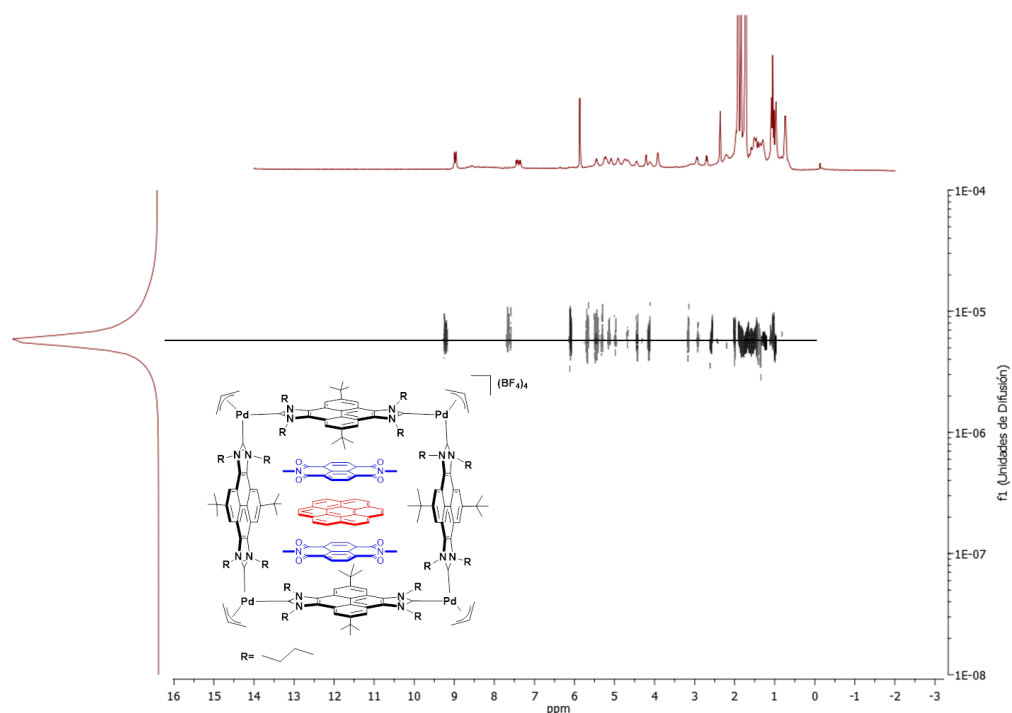


Figure S37. Selected region of DOSY NMR spectrum of $[3\supset(\text{coronene}+2\text{NTCDI})]^{4+}$ in CD_3CN at 298K. Diffusion Coefficient = $5.80 \times 10^{-6} \text{ (cm}^2/\text{s)} = 5.80 \times 10^{-10} \text{ (m}^2/\text{s)}$.

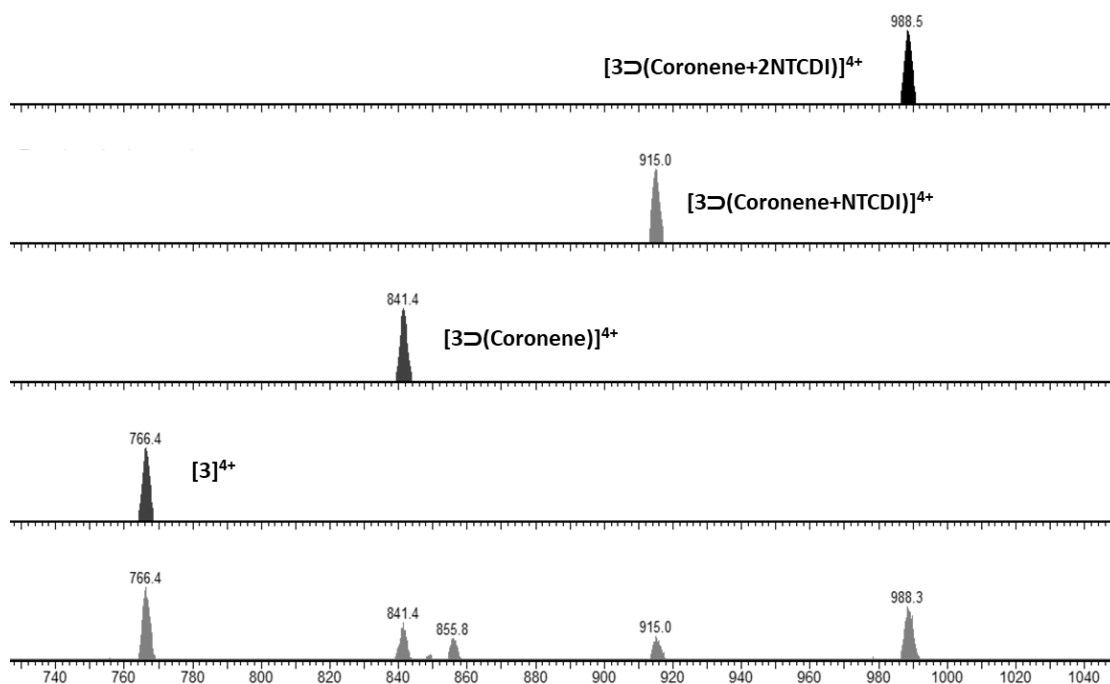


Figure S38. Selected region of the HRMS Spectrum of $[3\supset(\text{coronene}+2\text{NTCDI})]^{4+}$ in CD_3CN at 298K (bottom). The rest of spectra belong to the simulated spectra of $[3]^{4+}$, $[3\supset\text{Coronene}]^{4+}$, $[3\supset(\text{Coronene}+\text{NTCDI})]^{4+}$ and $[3\supset(\text{Coronene}+2\text{NTCDI})]^{4+}$.

4.- UV-Spectra

All UV-Vis spectra were carried out in CH₃CN at 298K. All spectra (Host and Host:Guest complexes) were recorded at a constant concentration of $1.65 \cdot 10^{-4}$ M.

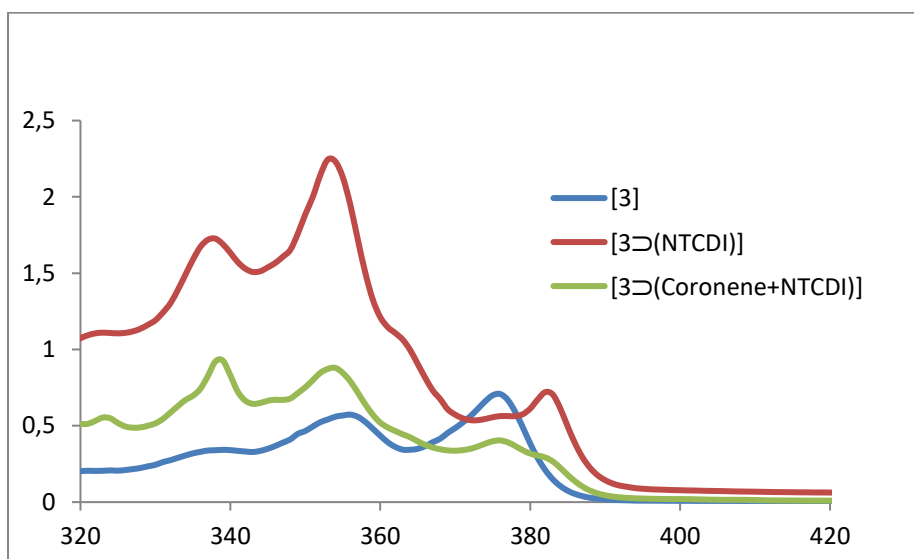


Figure S39. UV-Vis Spectra of [3](BF₄)₄; [3⊃(2NTCDI)] (BF₄)₄ and [3⊃(Coronene+2NTCDI)] (BF₄)₄ at constant concentration of $1.65 \cdot 10^{-4}$ M in CH₃CN at 298K.

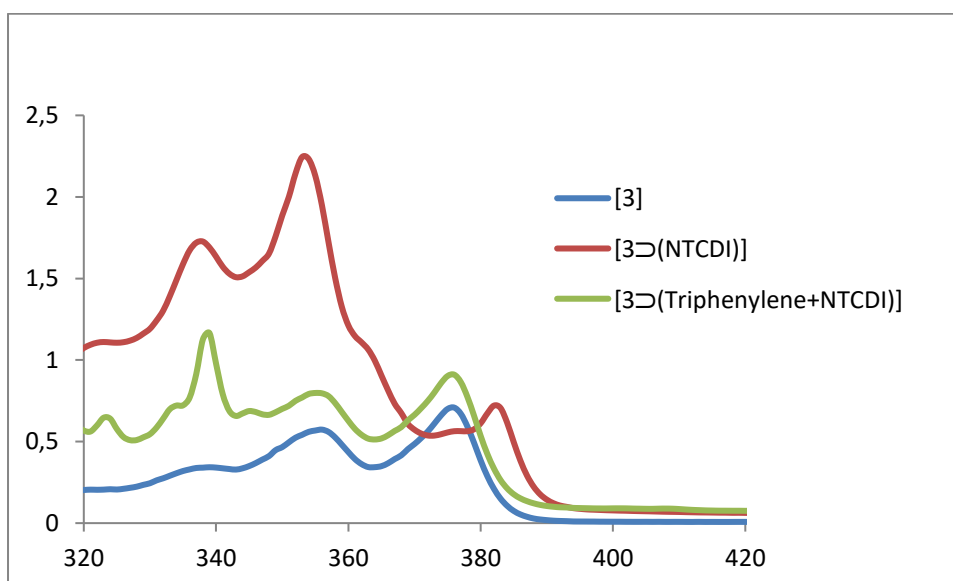


Figure S40. UV-Vis Spectra of [3](BF₄)₄; [3⊃(2NTCDI)](BF₄)₄ and [3⊃(triphenylene+2NTCDI)](BF₄)₄ at constant concentration of $1.65 \cdot 10^{-4}$ M in CH₃CN at 298K.

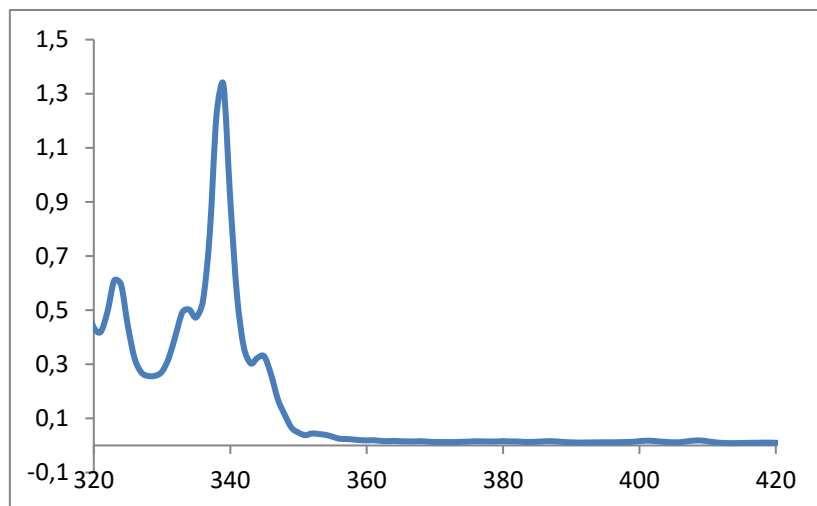


Figure S41. UV-Vis Spectrum of coronene $1.65 \cdot 10^{-4}$ M in CH_3CN at 298K.

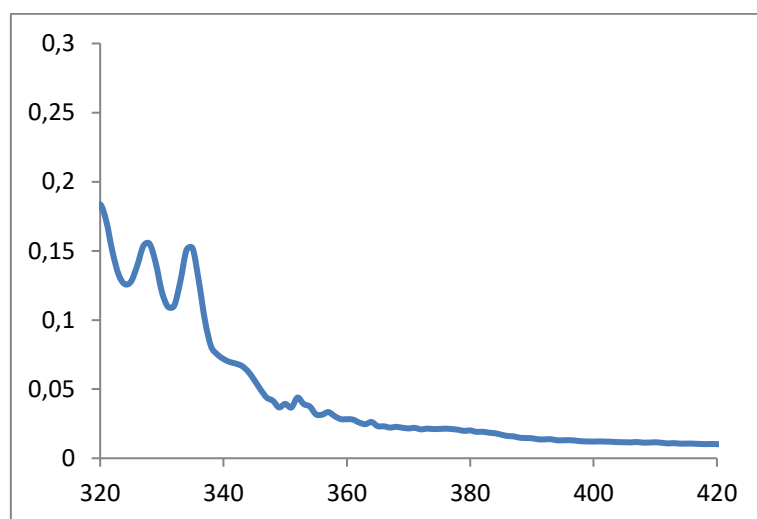


Figure S42. UV-Vis Spectrum of triphenylene $1.65 \cdot 10^{-4}$ M in CH_3CN at 298K.

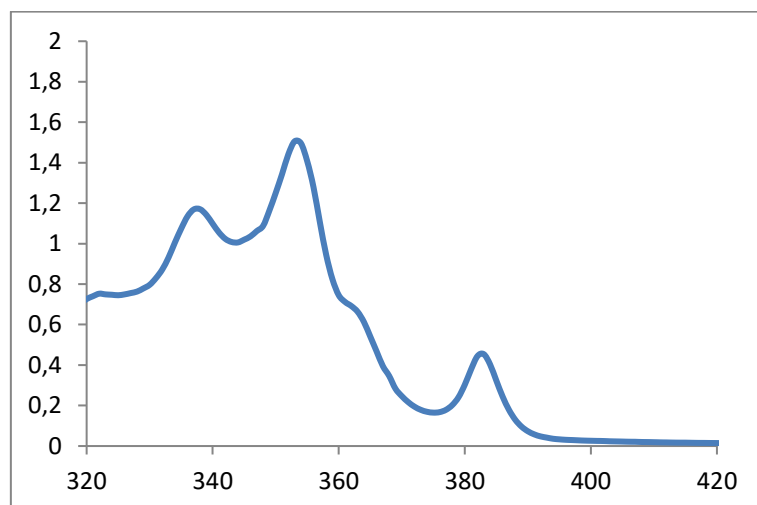


Figure S43. UV-Vis Spectrum of NTCDI $1.65 \cdot 10^{-4}$ M in CH_3CN at 298K.

5.- References

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- 2 a) A. J. Lowe, F. M. Pfeffer and P. Thordarson, *Supramol. Chem.*, 2012, **24**, 585-594; b) P. Thordarson, *Chem. Soc. Rev.*, 2011, **40**, 1305-1323.