Electronic Supplementary Information

Subtle structural engineering of coordination polymer host for the fluorescence modulation of host-guest donor-acceptor systems

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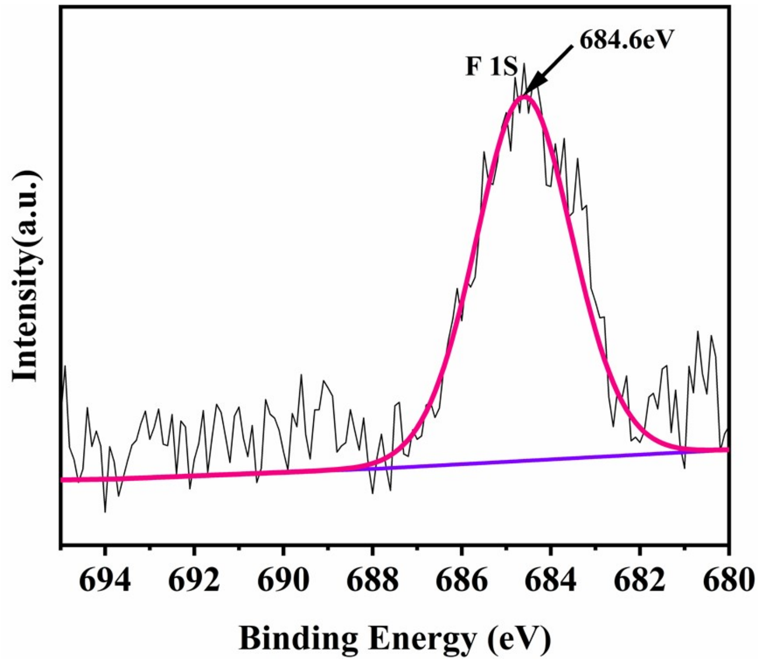


Fig. S1 The binding energy spectrum of F for **1.**

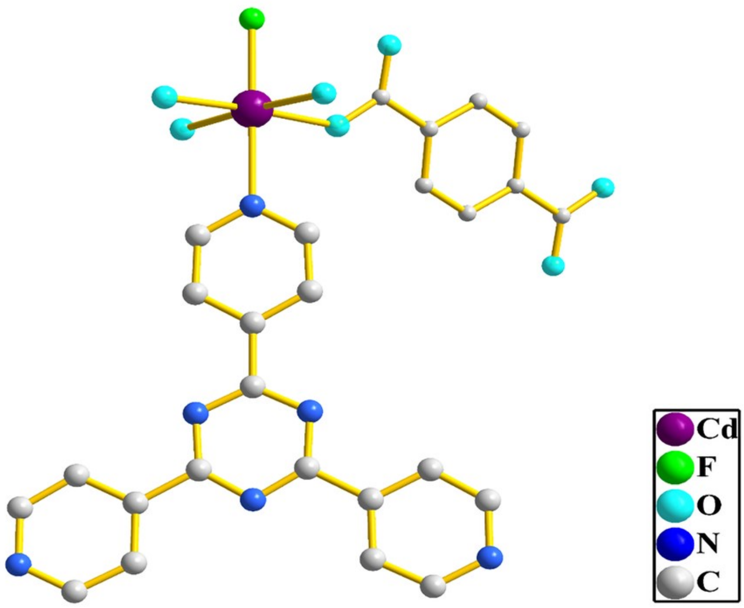


Fig. S2 Coordination environment of Cd (II) ions and ligand in complex **1**.

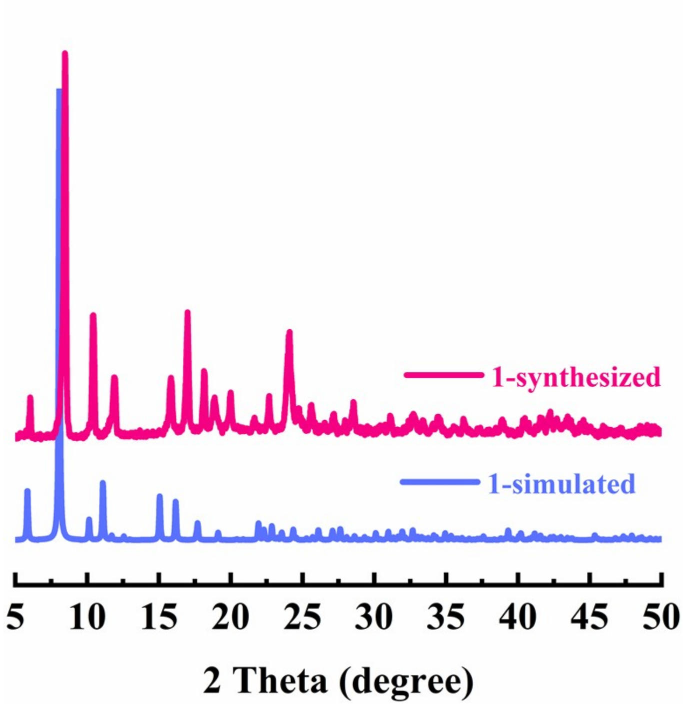


Fig. S3 The experimental and simulated PXRD patterns of sample **1**.

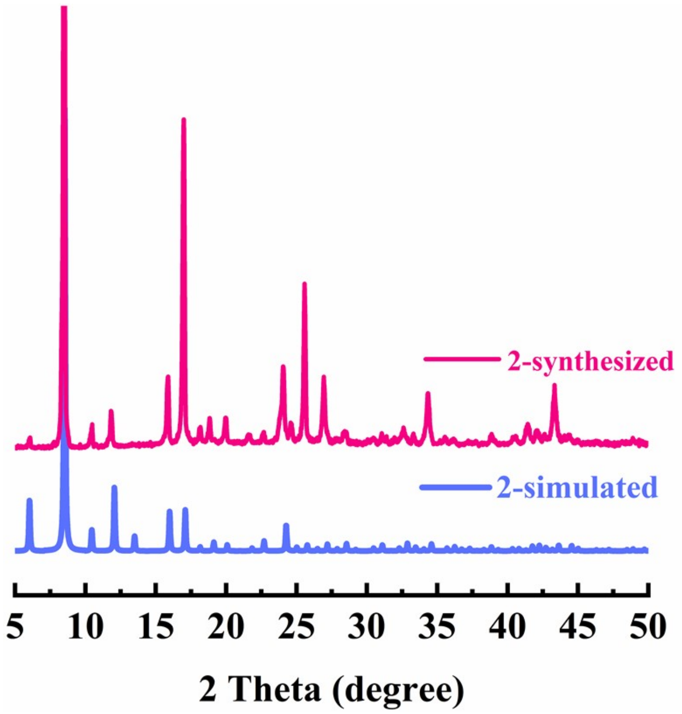


Fig. S4 The experimental and simulated PXRD patterns of sample **2**.

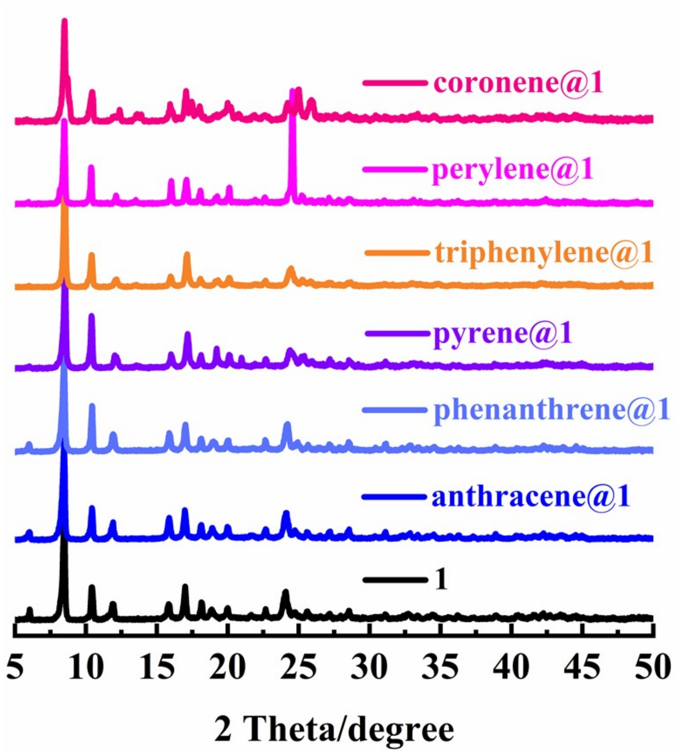


Fig. S5 The PXRD patterns of **1** and **PAHs@1**.

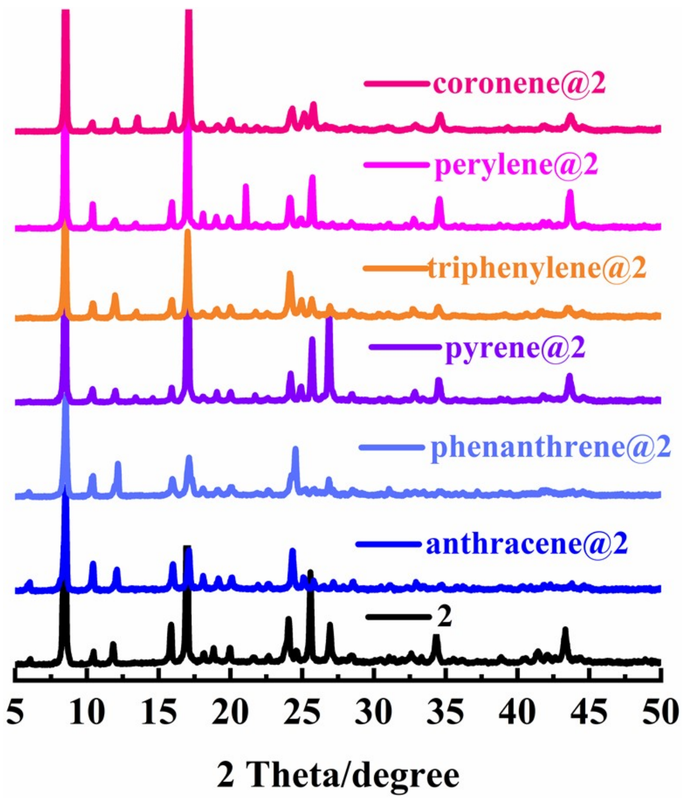


Fig. S6 The PXRD patterns of **2** and **PAHs@2**.

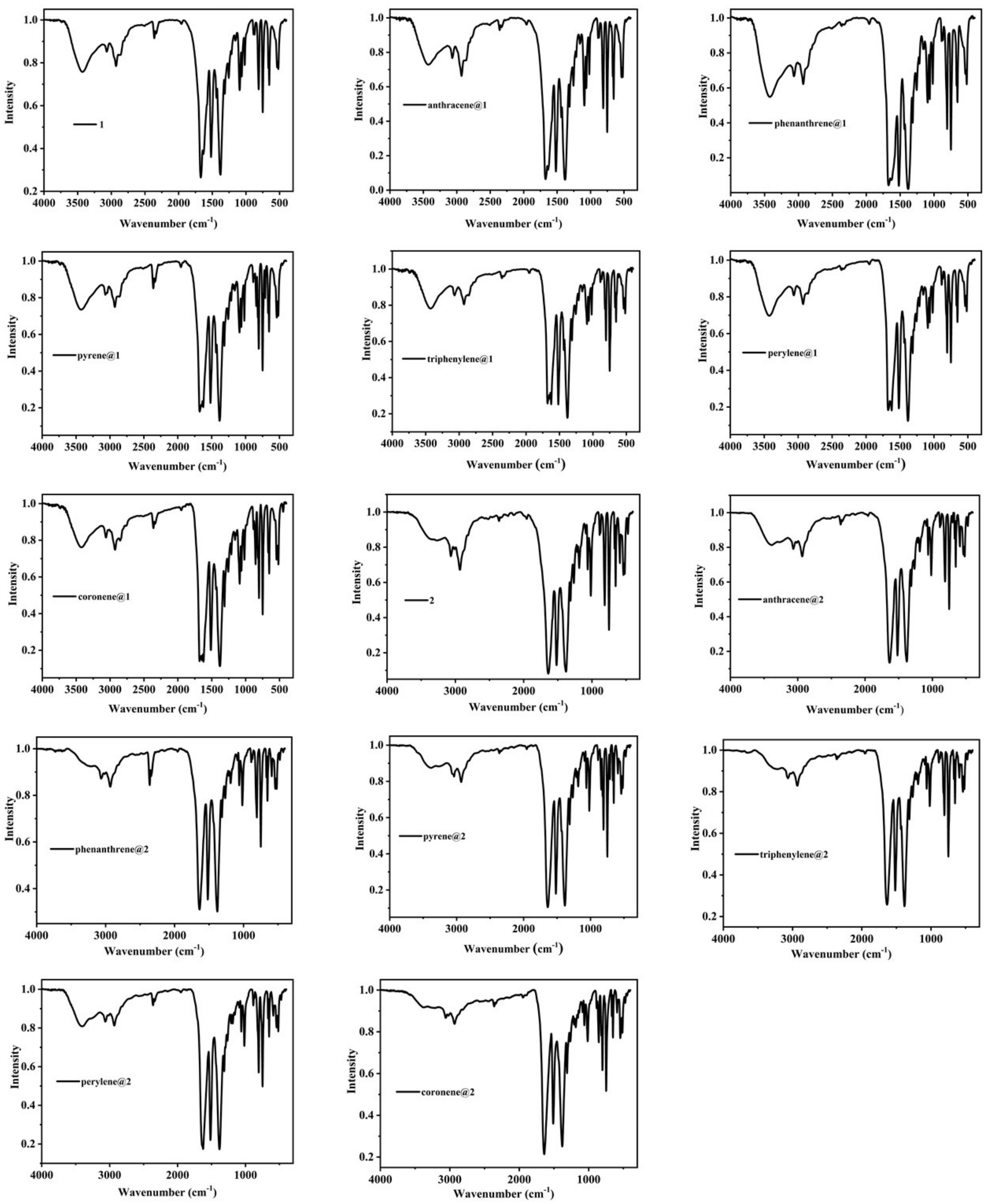


Fig. S7 Infrared spectroscopy of **1**, **2**, **PAHs@1** and **PAHs@2.**

Table S1 Crystal data and structure refinement parameters for the partial LCPs.

Compound	**1**	**2**
Formula	$C_{42}H_{24}Cd_3FN_6O_{12}$	$C_{42}H_{24}Zn_3FN_6O_{12}$
Formula weight	1160.92	1019.78
T (K)	175.57	286.9
Radiation (Å)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
Crystal system	Hexagonal	Hexagonal
space group	$P6_3$/mmc	$P6_3$/mmc
CCDC number	2099209	2283604
a (Å)	17.4307	16.9122
b (Å)	17.4307	16.9122
c (Å)	15.9206	14.6638
α (deg)	90	90
β (deg)	90	90
γ (deg)	120	120
V ($Å^3$)	4189.09	3632.26
Z	2	2
D (g/cm^{-3})	0.920	0.932
μ/mm^{-1}	6.373	1.533
F (000)	1134.0	1026
GOF on F^2	1.114	1.109
R_1, wR_2 [I > 2σ(I)]	R_1 = 0.0489, wR_2 = 0.1454	R_1 = 0.0533, wR_2 = 0.1320
R_1, wR_2 [all data]	R_1 = 0.0497, wR_2 = 0.1461	R_1 = 0.0551, wR_2 = 0.1331

$^aR_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $^bwR2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1}$

Compound	**perylene@1**	**perylene@2**
Formula	$C_{62}H_{36}Cd_3FN_6O_{12}$	$C_{62}H_{36}Zn_3FN_6O_{12}$
Formula weight	1413.22	1272.08
T (K)	100.00	100.01
Radiation (Å)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
Crystal system	Hexagonal	Hexagonal
space group	$P6_3$/mmc	$P6_3$/mmc
CCDC number	2099211	2099081
a (Å)	17.39990	16.91970
b (Å)	17.39990	16.91970
c (Å)	15.63180	14.57180
α (deg)	90	90
β (deg)	90	90
γ (deg)	120	120
V ($Å^3$)	4098.58	3612.68
Z	2	2
D (g/m^3)	1.145	1.169
μ/mm^{-1}	6.601	1.642
F (000)	1398.0	1290
GOF on F^2	1.115	1.107
R_1, wR_2 [I > 2σ(I)]	R_1 = 0.0670, wR_2 = 0.2192	R_1 = 0.0897, wR_2 = 0.2608
R_1, wR_2 [all data]	R_1 = 0.0680, wR_2 = 0.2203	R_1 = 0.0903, wR_2 = 0.2613

$^aR = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $^bwR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Compound	**triphenylene@1**
Formula	$C_{60}H_{36}Cd_3FN_6O_{12}$
Formula weight	1389.2
T (K)	107
Radiation (Å)	Cu K*α* (λ = 1.54184)
Crystal system	Hexagonal
space group	$P6_3/mmc$
CCDC number	2099210
a (Å)	17.38640
b (Å)	17.38640
c (Å)	15.72710
α (deg)	90
β (o)	90
γ (o)	120
V ($Å^3$)	4117.17
Z	2
D (g/m^3)	1.121
μ/mm^{-1}	6.563
F (000)	1374.0
GOF on F^2	1.174
R_1, wR_2 [I > 2σ(I)]	R_1 = 0.0576, wR_2 = 0.1807
R_1, wR_2 [all data]	R_1 = 0.0576, wR_2 = 0.1807

$^{a}R=\Sigma||F_o|-|F_c||/\Sigma|F_o|.^{b}wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

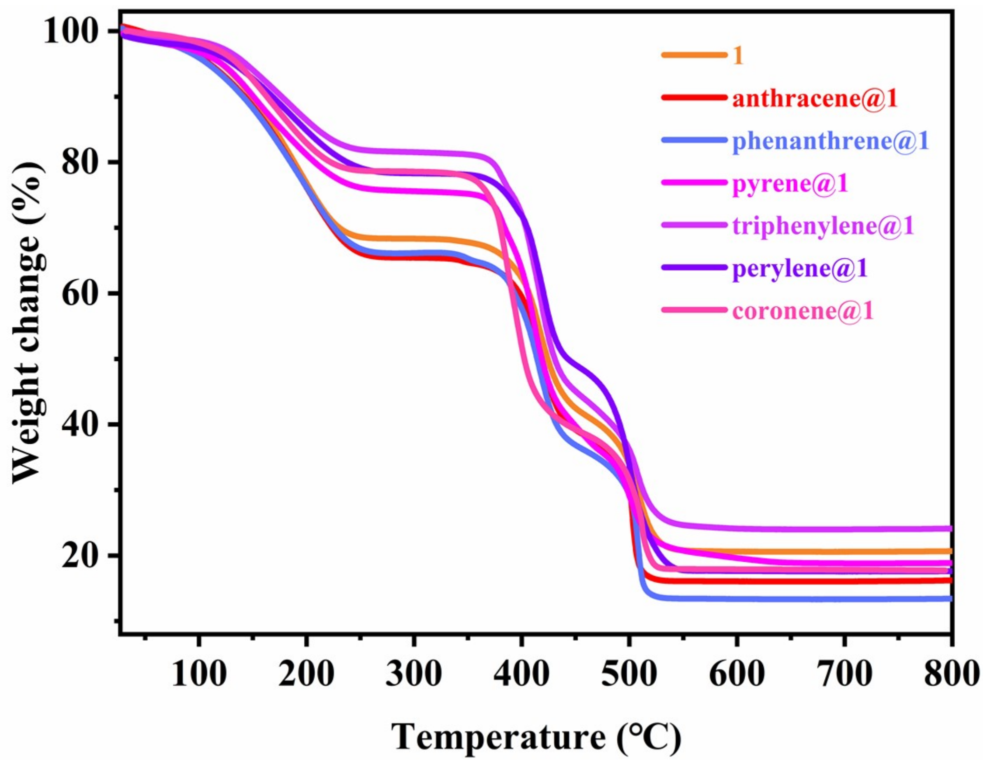


Fig. S8 The thermogravimetric curve of **1** and **PAHs@1** at air atmosphere.

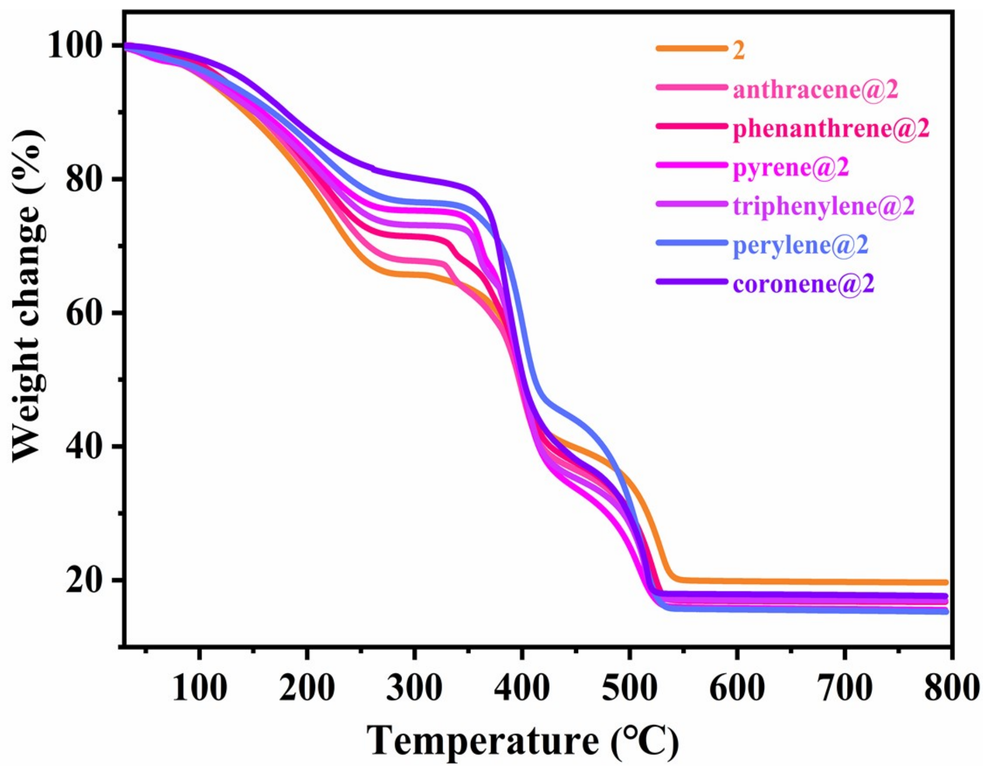


Fig. S9 The thermogravimetric curve of **2** and **PAHs@2** at air atmosphere.

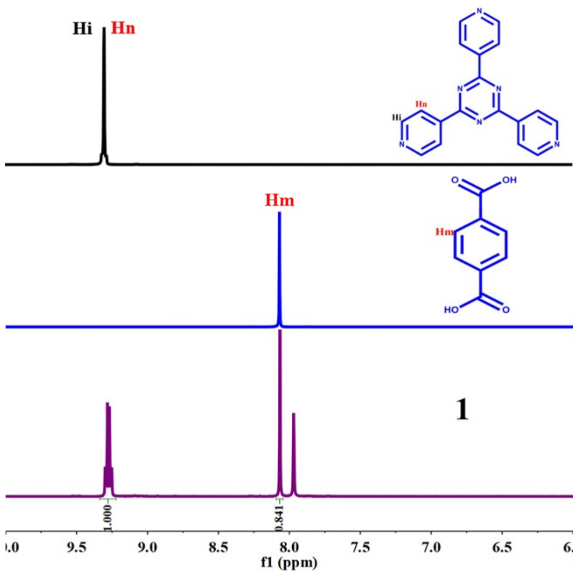


Fig. S10 The ^{1}H NMR spectra of digested **1** crystal samples and the corresponding ligands and guest.

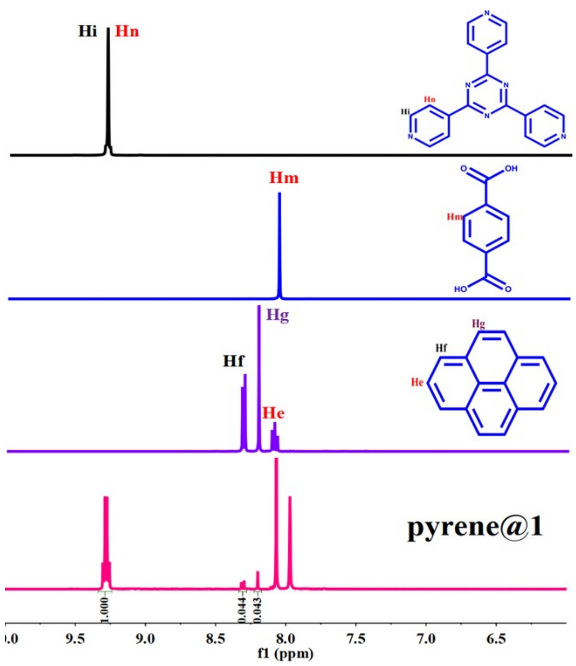


Fig. S11 The ^{1}H NMR spectra of digested **pyrene@1** crystal samples and the corresponding ligands and guest.

	Feeding amount of pyrene	Experimental ^{1}H integral area ratio for TPT to guest	Experimental TPT to guest molecular ratio	Loading ratio of pyrene
pyrene@1	0.025 mmol	1:0.044	7.58:1	13.2%

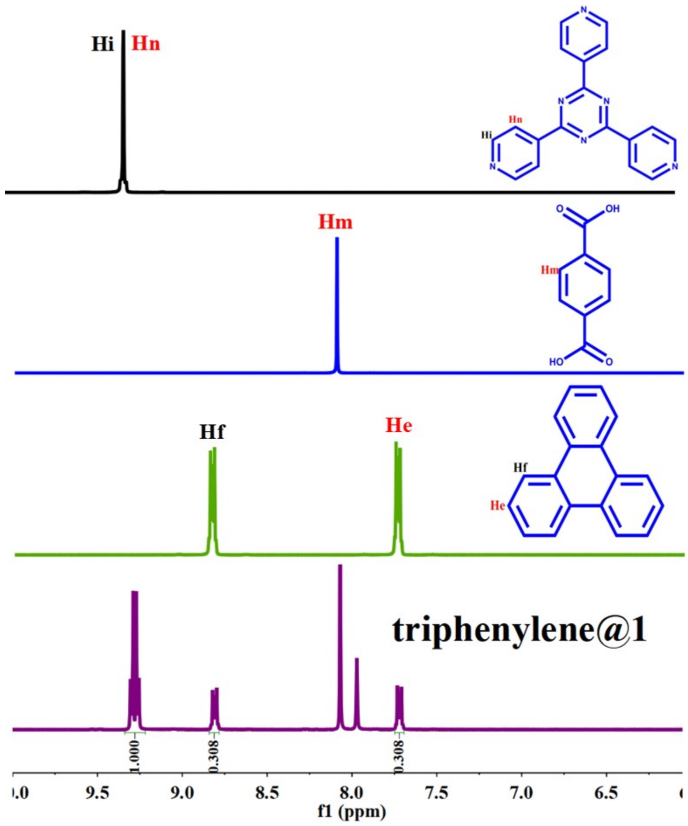


Fig. S12 The [1]H NMR spectra of digested **triphenylene@1** crystal samples and the corresponding ligands and guest.

	Feeding amount of triphenylene	Experimental ^{1}H integral area ratio for TPT to guest	Experimental TPT to guest molecular ratio	Loading ratio of triphenylene
triphenylene@1	0.025 mmol	1:0.308	1.62:1	61.7%

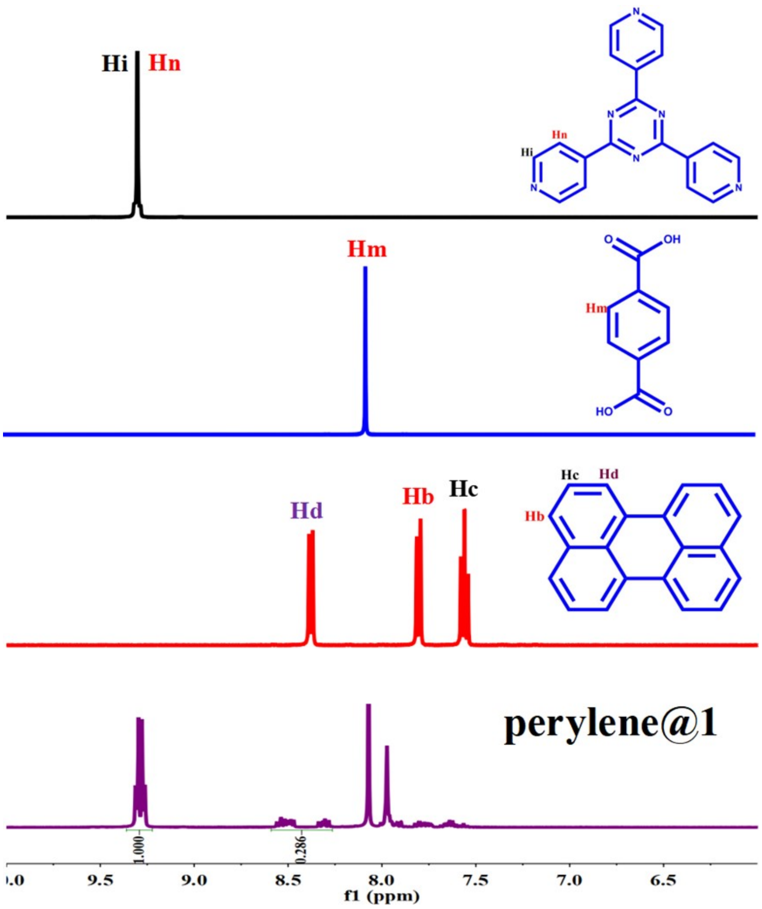


Fig. S13 The ^{1}H NMR spectra of digested **perylene@1** crystal samples and the corresponding ligands and guest.

	Feeding amount of perylene	Experimental ^{1}H integral area ratio for TPT to guest	Experimental TPT to guest molecular ratio	Loading ratio of perylene
perylene@1	0.025 mmol	1:0.286	1.17:1	85.4%

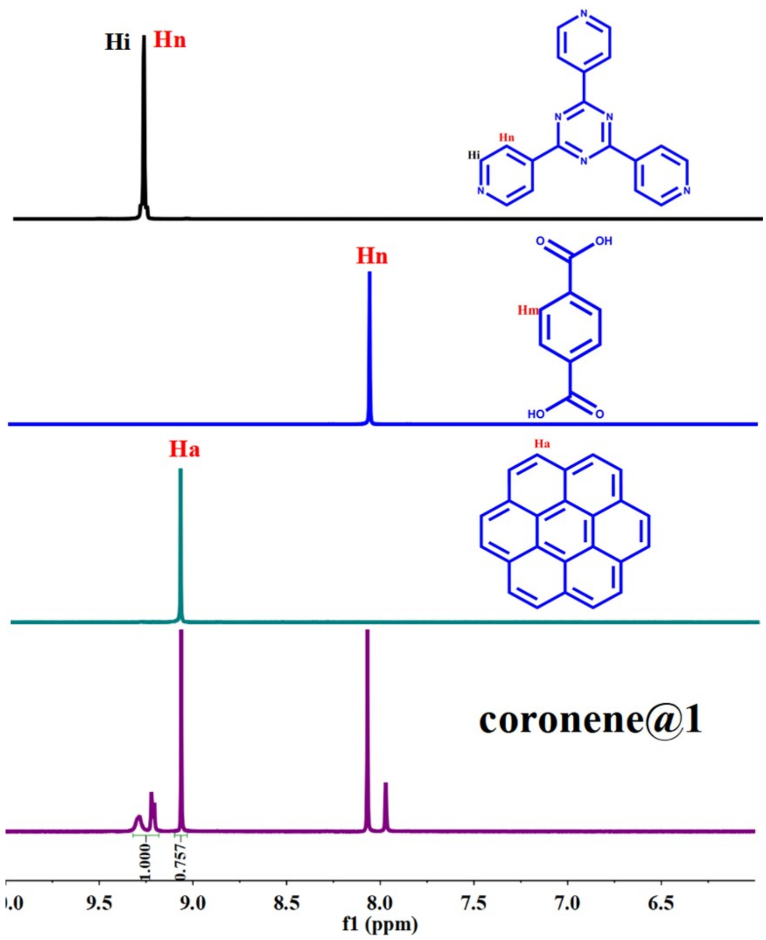


Figure. S14 The ^{1}H NMR spectra of digested **coronene@1** crystal samples and the corresponding ligands and guest.

coronene@1	Feeding amount of coronene	Experimental ^{1}H integral area ratio for TPT to guest	Experimental TPT to guest molecular ratio	Loading ratio of coronene
	0.025 mmol	1:0.757	1.32:1	75.8%

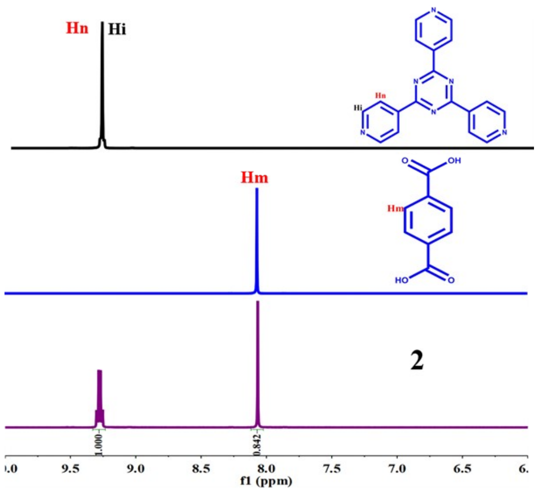


Fig. S15 The [1]H NMR spectra of digested **2** crystal samples and the corresponding ligands and guest.

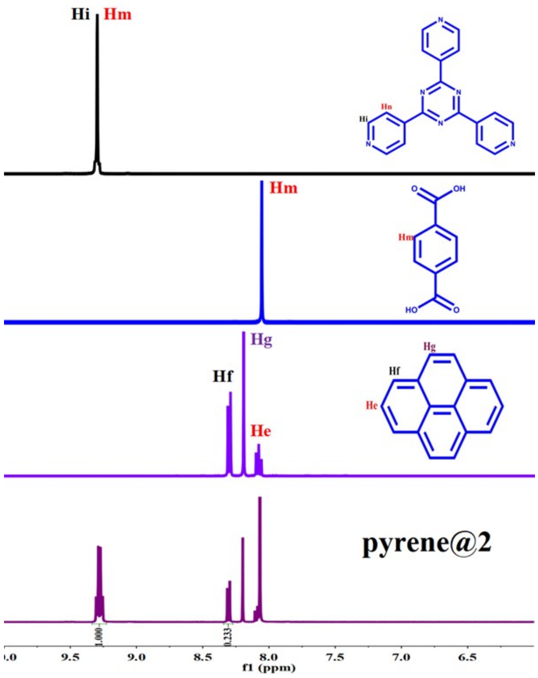


Fig. S16 The [1]H NMR spectra of digested **pyrene@2** crystal samples and the corresponding ligands and guest.

pyrene@2	Feeding amount of pyrene	Experimental [1]H integral area ratio for TPT to guest	Experimental TPT to guest molecular ratio	Loading ratio of pyrene
	0.025 mmol	1:0.233	1.43:1	69.9%

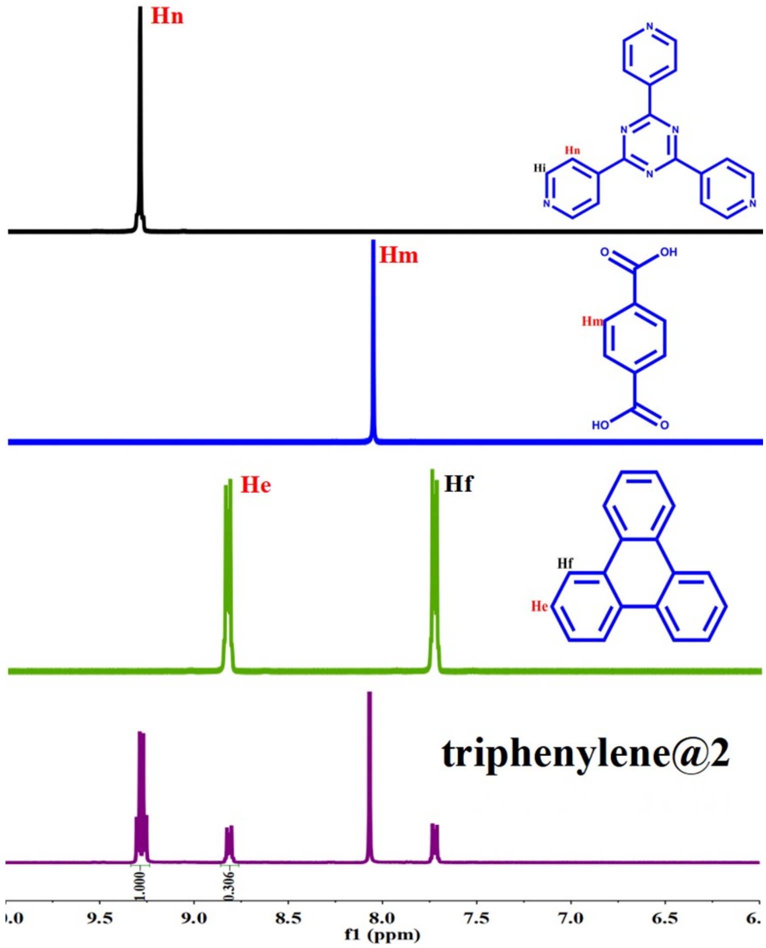


Fig. S17 The ^{1}H NMR spectra of digested **triphenylene@2** crystal samples and the corresponding ligands and guest.

triphenylene@2	Feeding amount of triphenylene	Experimental ^{1}H integral area ratio for TPT to guest	Experimental TPT to guest molecular ratio	Loading ratio of triphenylene
	0.025 mmol	1:0.306	1.63:1	61.3%

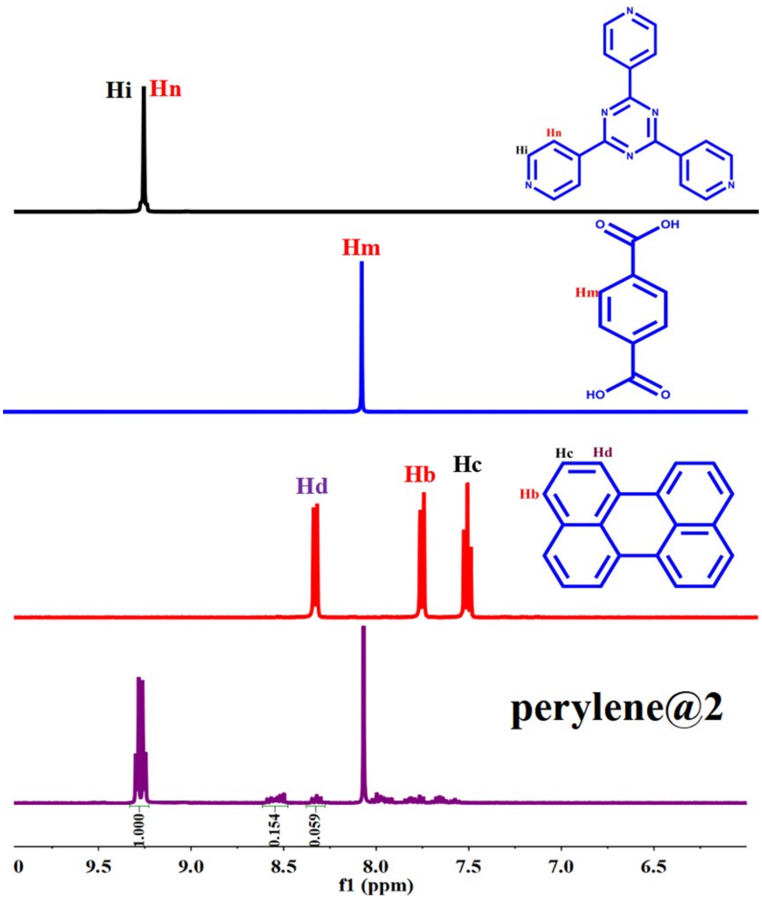


Fig. S18 The ^{1}H NMR spectra of digested **perylene@2** crystal samples and the corresponding ligands and guest.

perylene@2	Feeding amount of perylene	Experimental ^{1}H integral area ratio for TPT to guest	Experimental TPT to guest molecular ratio	Loading ratio of perylene
	0.025 mmol	1:0.213	1.56:1	63.9%

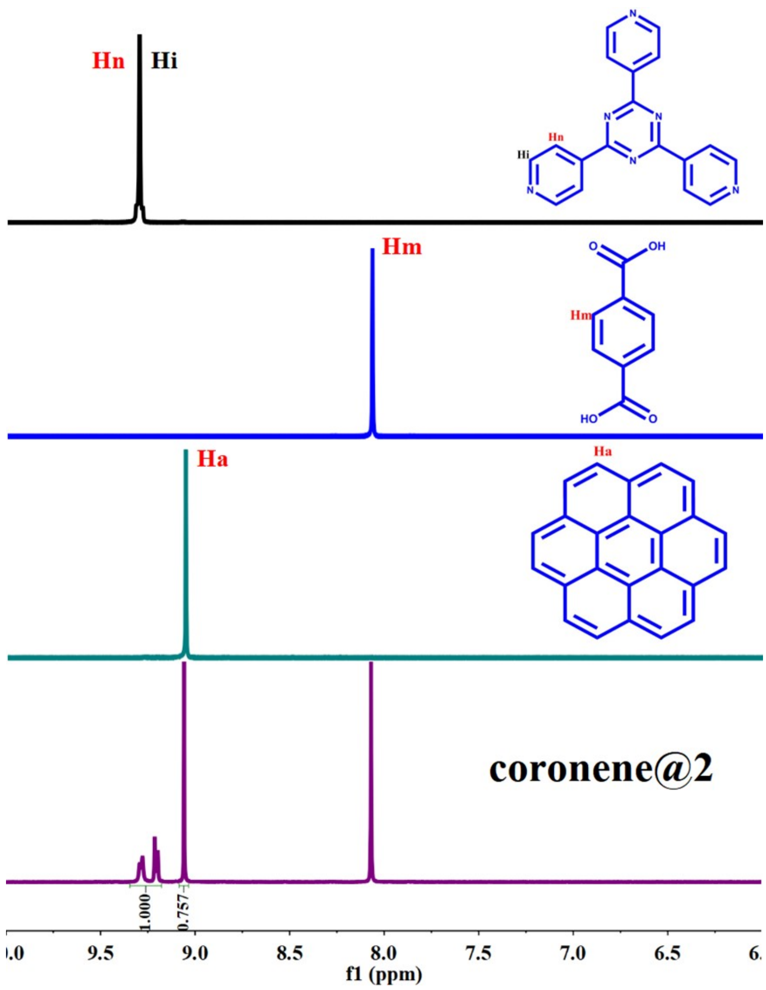


Fig. S19 The ^{1}H NMR spectra of digested **coronene@2** crystal samples and the corresponding ligands and guest.

	Feeding amount of coronene	Experimental ^{1}H integral area ratio for TPT to guest	Experimental TPT to guest molecular ratio	Loading ratio of coronene
coronene@2	0.025 mmol	1:0.757	1.32:1	75.7%

Table S2. Guest loading in **PAHs@1** and **PAHs@2**.

compound \ Guest loading (%) \ PAHs	pyrene	triphenylene	perylene	coronene
PAHs@1	13.2	61.7	85.4	75.8
PAHs@2	69.9	61.3	63.9	75.7

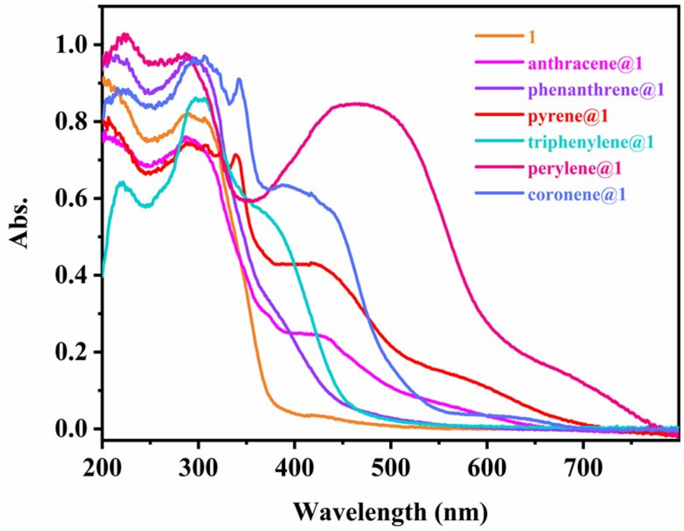


Fig. S20 UV-vis spectra of the complexes **1** and **PAHs@1**.

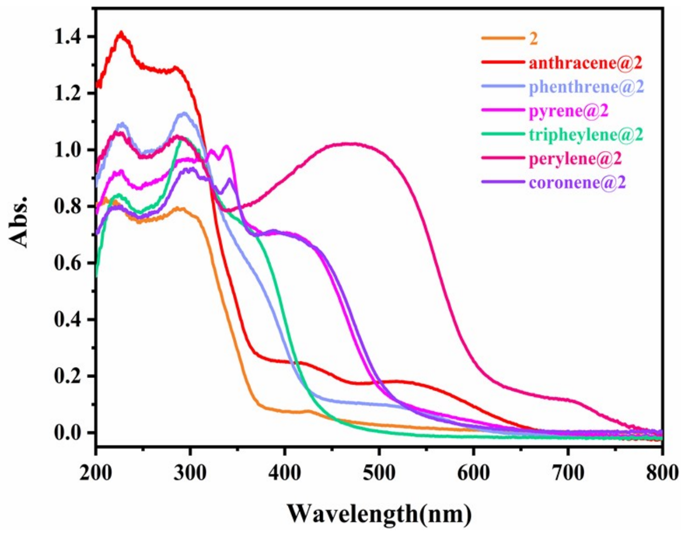


Fig. S21 UV-vis spectra of the complexes **2** and **PAHs@2**.

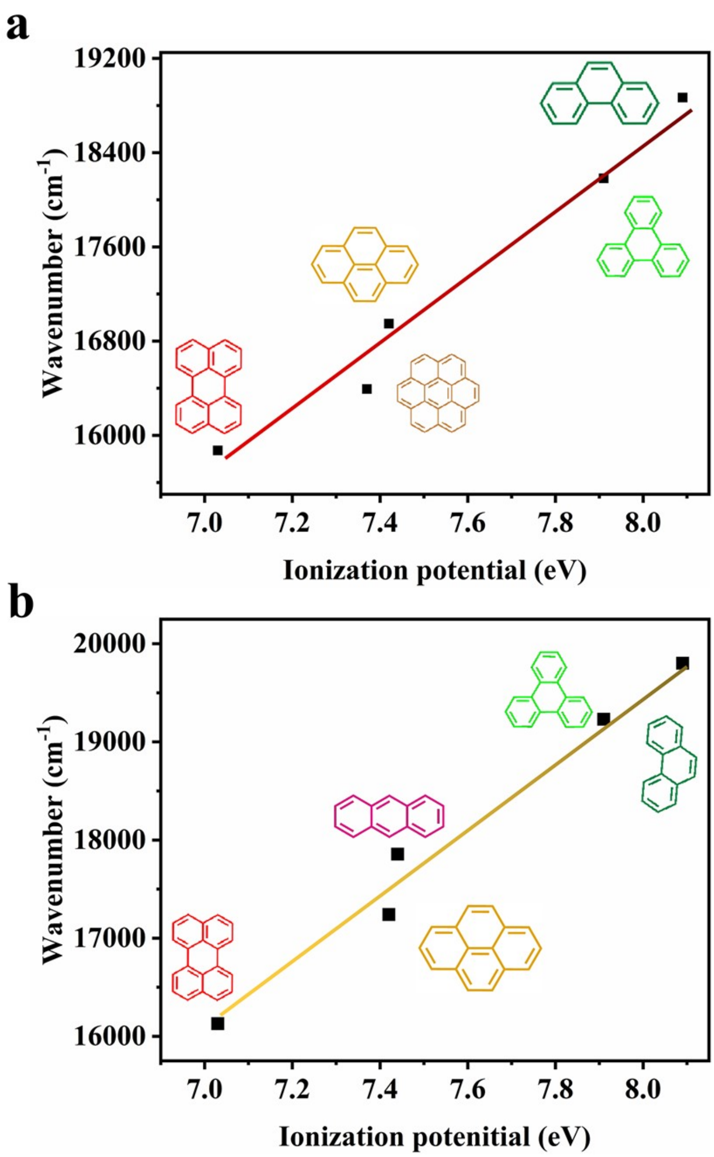
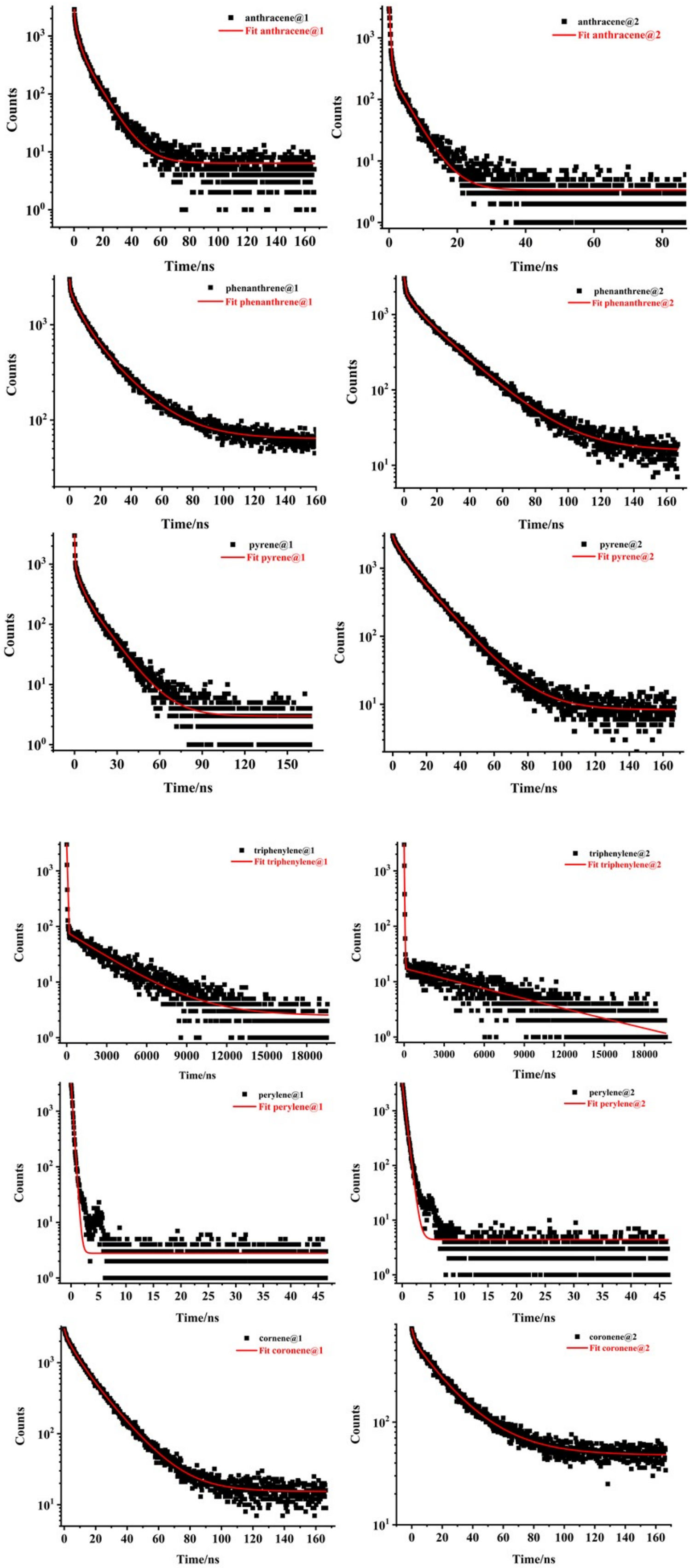


Fig. S22 Linear correlation between the wavenumber of **PAHs@1** (a) and **PAHs@2** (b) and the ionization potential (IP) of corresponding guests. (Ionization potential data obtained from ref [1-4])


anthracene@1
Fit anthracene@1
anthracene@2
Fit anthracene@2
phenanthrene@1
Fit phenanthrene@1
phenanthrene@2
Fit phenanthrene@2
pyrene@1
Fit pyrene@1
pyrene@2
Fit pyrene@2
triphenylene@1
Fit triphenylene@1
triphenylene@2
Fit triphenylene@2
perylene@1
Fit perylene@1
perylene@2
Fit perylene@2
cornene@1
Fit coronene@1
coronene@2
Fit coronene@2
Counts
Time/ns

Complex	τ (ns)	average τ (ns)	χ^2
anthracene@1	τ_1=1.40 τ_2= 6.06 τ_3=16.04	τ =9.04	1.3239
phenanthrene@1	τ_1=1.41 τ_2= 10.37 τ_3=26.26	τ=19.85	0.9562
pyrene@1	τ_1=0.21 τ_2= 3.84 τ_3=14.09	τ=10.39	0.9747
triphenylene@1	τ_1=17.90 τ_2= 2980.50	τ=2326.95	1.0552
perylene@1	τ_1= 0.24 τ_2= 1.75 τ_3=50.00	τ=2.16	1.1464
coronene@1	τ_1=1.32 τ_2= 8.51 τ_3=17.40	τ=14.24	0.9858
anthrene@2	τ_1=0.26 τ_2= 2.50 τ_3=8.32	τ=3.18	1.0455
phenanthrene@2	τ_1=0.40 τ_2= 5.13 τ_3=22.20	τ=20.34	1.0218
pyrene@2	τ_1=1.08 τ_2= 5.96 τ_3=15.55	τ=14.24	1.0118
triphenylene@2	τ_1=16.55 τ_2=71.01 τ_3=5186.66	τ=3010.52	0.9949
perylene@2	τ_1=0.42 τ_2= 2.00	τ=0.7	1.0820
coronene@2	τ_1=2.91 τ_2= 22.14	τ=21.37	0.9668

Fig. S23 Emission decay traces and fits results of the fluorescent lifetime (τ) for complexes **PAHs@1** and **PAHs@2** at room temperature.

Table S3. Summary of crystallographic parameter data for LCPs**.**

code	a/Å	b/Å	c/Å	α/°	β/°	γ/°
1	17.4307	17.4307	15.9206	90	90	120
anthracene@1	17.389	17.389	15.736	90	90	120
phenanthrene@1	17.3916	17.3916	15.7466	90	90	120
pyrene@1	17.3925	17.3925	15.6977	90	90	90
triphenylene@1	17.3864	17.3864	15.7271	90	90	120
perylene@1	17.399	17.399	15.631	90	90	120
2	16.9122	16.9122	14.6638	90	90	120
anthracene@2	16.9003	16.9003	14.4398	90	90	120
phenanthrene@2	16.9225	16.9225	14.4953	90	90	120
pyrene@2	16.90	16.90	14.394	90	90	120
triphenylene@2	16.8914	16.8914	14.5020	90	90	120
perylene@2	16.9197	16.9197	14.5718	90	90	120
coronene@2	16.919	16.919	14.162	90	90	120

References

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2. J. B. Birks and M. A. Slifkin, π-Electronic Excitation and Ionization Energies of Condensed Ring Aromatic Hydrocarbons, *Nature*, 1961, **191**, 761-764.
3. F. Brogli and E. Heilbronner, The Photoelectron Spectra of Benzenoid Hydrocarbons $C_{18}H_{12}$, *Angew. Chem. Int. Ed.*, 1972, **11**, 538-539.
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