-Electronic Supporting Information-

Supramolecular control over recognition and efficient detection of picric acid

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I- Synthesis and characterization

I-1 General procedures

All the syntheses were run under a nitrogen atmosphere. Solvents used for those preparations were distilled under N_2 and stored over molecular sieves. All the starting materials were commercially available and used as received. (3-Formyl-4-hydroxy)benzyl phenolate and (3-formyl-4-hydroxy)benzyl *tert*-butanoate were prepared as already reported.[1,2] Elemental C, H and N analyses were performed on a Perkin-Elmer 2400 II analyzer on freshly prepared and isolated samples. ^{1}H NMR spectra were recorded using Avance 400 Brüker spectrometer with working frequencies respectively at 400 MHz for ^{1}H. Chemical shifts were referenced to the residual proton resonance of the deuterated solvents. IR spectra were recorded in the 4000-600 cm^{-1} region with a Perkin-Elmer Spectrum 100 FTIR using the ATR mode.

I-2 Synthesis of $[Al_2L^{Ph}(H_2O)_4(NO_3)_2]\cdot 10H_2O$ (abbreviated **1** for the cationic part)

(3-Formyl-4-hydroxy)benzyl phenolate (170 mg; 0.702 mmol) and 1,2,4,5-phenylenetetramine hydrochloride (62.3 mg; 0.176 mmol) were suspended in 70 mL of tetrahydrofuran and 30 mL of methanol. Then, triethylamine (196 µL; 1.405 mmol) was added. The resulting solution was heated at 60°C for 30 minutes. A solution of $Al(NO_3)_3.9H_2O$ (198 mg; 0.528 mmol) in 17 mL of methanol was dropwise added to the previous solution. The reaction mixture was gently refluxed for 2 days. After cooling down to room temperature, solvents were removed under vacuum. The red solid obtained was stirred in water for 2h and filtered. The solid was then triturated in acetonitrile, filtered, and dried with diethylether. The crude product was purified by crystallization from a concentrated ethanol solution. $[Al_2L^{Ph}(H_2O)_4(NO_3)_2]\cdot 10H_2O$ (144 mg, 52%). Anal. Calc. for $C_{62}H_{46}N_6O_{22}Al_2.10H_2O$: C, 50.96; H, 4.55; N, 5.75; Found: C, 50.76; H, 4.29 N, 6.03; ^{1}H NMR (400 MHz DMSO-d_6, ppm): δ 9.76 (s, 4H, *H*C=N), 9.02 (s, 2H, Ar-*H*), 8.70 (s, 4H, Ar-*H*), 8.28 (d, 4H, Ar-*H)*, 7.49 (t, 8H, Ar-*H*), 7.35-7.27 (t + d, 12H, Ar-*H*), 7.20 (d, 4H, Ar-*H*); IR (ATR, cm^{-1}): ν 1725 (s, C=O, 1607 (s, C=N).

I-3 Synthesis of $[Al_2L^{tBu}(H_2O)_4(NO_3)_2]\cdot 8H_2O$ (abbreviated **2** for the cationic part)

(3-Formyl-4-hydroxy)benzyl *tert*-butanoate (211.6 mg; 0.953 mmol) and 1,2,4,5-phenylenetetramine hydrochloride (84.6 mg; 0.238 mmol) were suspended in 96 mL of tetrahydrofuran and 40 mL of methanol. Then, triethylamine (270 µL; 1.94 mmol) was added. The resulting solution was heated at 60°C for 30 minutes. A solution of $Al(NO_3)_3.9H_2O$ (266.6 mg; 0.711 mmol) in 16 mL of methanol was dropwise added to the previous solution. The reaction mixture was gently refluxed for 2 days. After cooling down to room temperature, solvents were removed under vacuum. The red solid obtained was stirred in water for 4h, filtered and dried under vacuum. The solid was then triturated in diethyl ether, and filtered. The crude product was purified by crystallization from a concentrated ethanol solution. $[Al_2L^{tbu}(H_2O)_4(NO_3)_2]\cdot 8H_2O$ (192 mg, 60%). Anal Calc. for $C_{54}H_{62}N_6O_{22}Al_2.8H_2O$: C, 48.22; H, 5.84; N, 6.25; Found: C, 48.07; H, 6.07; N, 6.14; ^{1}H NMR (400 MHz DMSO-d_6, ppm): δ 9.54 (s, 4H, *H*C=N), 8.87 (s, 2H, Ar-*H*), 8.37 (s, 4H, Ar-*H)*, 8.07 (d, 4H, Ar-*H*), 7.10 (d, 4H, Ar-*H*), 1.59 (s, 36H, C(C*H*$_3$)$_3$); IR (ATR, cm^{-1}): ν 1714 (s, C=O), 1613 (s, C=N).

I-4 Synthesis of $[Al_2L(H_2O)_4(NO_3)_2]\cdot 2H_2O$ (abbreviated **3** for the cationic part)

$H_2L\cdot 0.5H_2O$: 1,2,4,5-Phenylenetetramine hydrochloride (200 mg; 0.70 mmol) and 2-hydroxybenzaldehyde (340 mg; 2.79 mmol) were suspended in 25 mL of dry and degassed acetonitrile. Triethylamine (0.8 mL; 5.60 mmol) was then added. The resulting red solution was stirred at room temperature for 3h. After evaporation of the solvent, the obtained solid was washed with ethanol and dried with diethylether, to yield

$H_2L \cdot 0.5H_2O$ (244 mg, 62%) as an orange solid. Anal. Calc. for $C_{34}H_{26}N_4O_4.0.5H_2O$: C, 72.46; H, 4.83; N, 9.94; Found: C, 72.55; H, 4.45; N, 10.12; ^{1}H NMR (400 MHz DMSO-d_6, ppm): δ 9.12 (s, 4H, *H*C=N), 7.71 (s, 6H, Ar-*H*), 7.46 (m, 4H, Ar-*H*), 7.02 (m, 8H, Ar-*H*); IR (ATR, cm^{-1}): ν 1604 (s, C=N).

$[Al_2L(H_2O)_4(NO_3)_2]\cdot 2H_2O$: $H_2L \cdot 0.5H_2O$ (203 mg; 0.361 mmol) was suspended in 15 mL of ethanol. A solution of $Al(NO_3)_3.9H_2O$ (412 mg; 1.098 mmol) in 5 mL of ethanol was slowly added to the suspension of the ligand. The reaction mixture was refluxed for 5h and then stirred at room temperature overnight. The solid obtained was isolated by filtration and washed several time with acetone. The crude product was purified by crystallization from a concentrated solution in ethanol. $[Al_2L(H_2O)_4(NO_3)_2]\cdot 2H_2O$ (199 mg, 65%). Anal. Calc. for $C_{34}H_{30}N_6O_{14}Al_2.2H_2O$: C, 48.81; H, 4.10; N, 10.05; Found: C, 48.60; H, 4.19; N, 9.86; ^{1}H NMR (400 MHz DMSO-d_6, ppm): δ 9.38 (s, 4H, *H*C=N), 8.73 (s, 2H, Ar-*H*), 7.70 (d, 4H, Ar-*H*), 7.59 (t, 4H, Ar-*H*), 7.02 (d, 4H, Ar-*H*), 6.93 (t, 4H, Ar-*H*); IR (ATR, cm^{-1}): ν 1606 (s, C=N).

I-5 Synthesis of **1.PA**

$[Al_2L^{ph}(H_2O)_4(NO_3)_2]\cdot 10H_2O$ (11 mg; 7.53×10^{-3} mmol) was solubilized in 10 mL of methanol. The solution of picric acid (108 mg; 281×10^{-3} wih purity of 59.5%) in 10 mL of methanol was carefully layered on the top of the solution of **1**. The tube was sealed and left undisturbed. After one week orange crystals were collected for X-Ray diffraction studies. **1.PA** (15 mg, 85%). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 9.61 (s, 4H, *H*C=N), 8.88 (s, 2H, Ar-*H*), 8.65 (s, 4H, Ar-*H*), 8.58 (s, 4H, PA), 8.29 (d, 4H, Ar-*H),*7.49 (t, 8H, Ar-*H*), 7.33 (t, 4H, Ar-*H*), 7.28 (d, 8H, Ar-*H*), 7.21 (d, 4H, Ar-*H*); IR (ATR, cm^{-1}): ν 1719 (s, C=O), 1609 (s, C=N), 1361 (m, C-O PA).

II- X-Ray crystallography

Data collection and structure refinement

Intensity data were collected at low temperature on Gemini Oxford Diffraction (**1**, CuKα radiation), SuperNova Agilent (**1.PA**, CuKα radiation) or Apex2 Quazar Bruker (**3**, MoKα radiation) diffractometers. Structures were solved using SUPERFLIP[3] and refined by full-matrix least squares procedures on F using the programs of the PC version of CRYSTALS.[4] All non hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Atomic scattering factors were taken from the International Tables for X-ray Crystallography.[5] For compounds **1** and **1.PA**, disorders were treated. It was not possible to resolve diffuse electron-density residuals (enclosed solvent molecules). Treatment with the SQUEEZE facility from PLATON[6] resulted in a smooth refinement.

Table S1. *Crystallographic and refinement data for **1**, **1.PA**, and **3***

Compound	**1**	**1.PA**	**3**
Empirical formula	$C_{62}H_{44}Al_2N_4O_{16}$	$C_{78}H_{58}Al_2N_{10}O_{30}$	$C_{40}H_{54}Al_2N_6O_{20}$
Formula weight	1155.02	1669.33	992.86
Temperature (K)	100	100	100
Wavelength (Å)	1.54180	1.54180	0.71073
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P -1	P -1	P -1
Unit cell dimensions (Å, °)	a = 11.8503(5) b = 12.3444(5) c= 14.6936(6) α = 104.263(3) β = 90.576(3) γ = 105.922(3)	a = 11.8132(5) b= 15.0997(7) c= 25.2353(3) α = 96.757(2) β = 96.333(2) γ = 108.853(4)	a = 9.3142(15) b= 11.3130(17) c= 11.6842(19) α = 74.397(7) β = 88.276(7) γ = 70.465(6)
Volume ($Å^3$)	1996.29(4)	4177.2(3)	1115.1(3)
Z	1	2	1
Density (calculated)	0.961	1.327	1.48
Absorption coefficient (mm^{-1})	0.781	1.070	0.154
F(000)	592	1716	522
Crystal size (mm^3)	0.05 x 0.20 x 0.25	0.06 x 0.08 x 0.44	0.02 x 0.15 x 0.20
Theta range for data collection (°)	3.855-61.473	3.134-80.283	1.814-25.571
Index ranges	-13<=h<=+13 -14<=h<=+13 0<=h<=+16	-14<=h<=+14 -19<=h<=+18 0<=h<=+31	-11<=h<=+12 -13<=h<=+13 -14<=h<=+14
Reflections collected	25515	117969	15596
Independent reflections	6151 (Rint = 0.027)	17074 (Rint = 0.111)	4085(Rint = 0.062)
Absorption correction	Multi-scan	Gaussian	Multi-scan
Refinement method	Least squares procedures on F	Least squares procedures on F	Least squares procedures on F
Data / restraints / parameters	5036 / 0 / 373	11116 / 8 / 1081	4311 / 0 / 307
Goodness-of-fit on F	1.074	1.059	1.1292
R [I> nσ(I)]	0.0636 (n=3)	0.0817 (n=1.9)	0.0643 (n=2)
*w*R [I> nσ(I)]	0.0797 (n=3)	0.0885 (n=1.9)	0.0652 (n=2)
Largest diff. peak and hole (e $Å^{-3}$)	-0.26, +1.50	-0.60, +1.17	-0.59, +0.98

$R = \Sigma[|Fo-Fc|]/\Sigma[|Fo]$

$wR = (\Sigma[|w| \ |Fo|-|Fc] \ |^2|]/\Sigma[|wFo^2|])^{1/2}$

Fig. S1 *Ortep view of the asymmetric unit in* ***1*** *with ellipsoids cut at the 30% level (H atoms, methanol solvent molecules and nitrate ions have been omitted for clarity).*

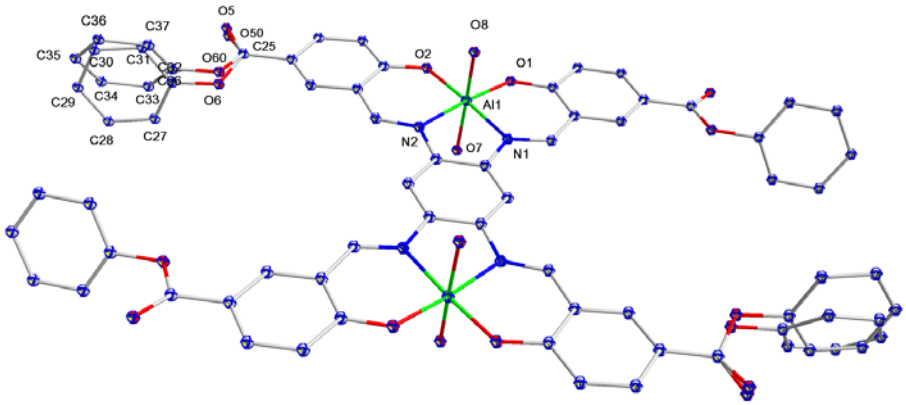


Fig. S2 *Ortep view of the asymmetric unit in* ***3*** *with ellipsoids cut at the 30% level (H atoms, methanol solvent molecules and nitrate ions have been omitted for clarity).*

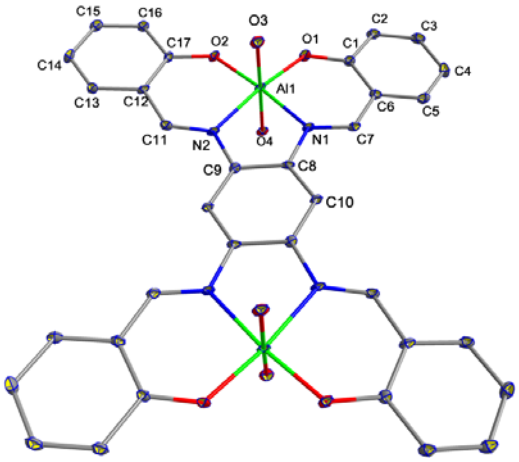
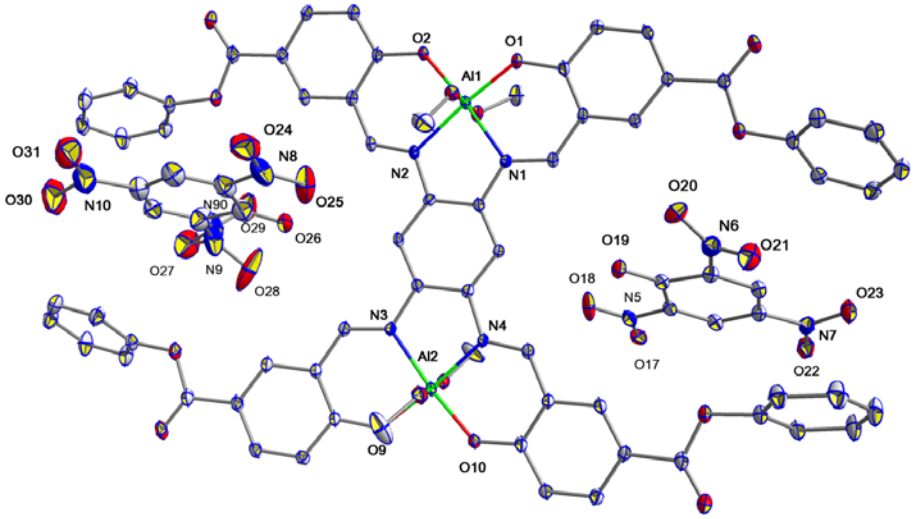


Fig. S3 *Ortep view of the asymmetric unit in* ***1.PA*** *with ellipsoids cut at the 30% level. (H atoms have been omitted for clarity).*



III- Spectroscopic measurements

III-1 Absorption and emission measurements

UV-visible spectra were recorded with a Perkin Elmer Lambda 35 spectrophotometer. Measurements were made in 1 cm path length quartz cells at 293 K. Emission spectra were measured using a Horiba-Jobin Yvon FluoroMax-4 spectrofluorimeter, equipped with three-slit double-grating excitation and emission monochromators. The steady-state luminescence was excited by unpolarized light from a 150 W continuous-wave xenon lamp and detected at an angle of 90° for diluted solution measurements (1 cm quartz cell) by a red-sensitive Hamamatsu R228 photomultiplier tube. Spectra were reference-corrected for both the excitation source light-intensity variation (lamp and grating) and the emission spectral response (detector and grating).

The quantum yields for fluorescence in solution were determined using a NaOH 0.1 mol L^{-1} solution of fluoresceine with λ_{exc} = 470 nm for standard and samples. Concentrations of the solutions, included solutions of standard, were adjusted so that the absorbance at λ_{ex} (470 nm) was between 0.04 and 0.05. In this case, intensity of the measured emission can be considered to be proportional to the concentration of the species in solution. The emission quantum yields were then calculated using the equation below, where ϕ_s is the emission quantum yield of the sample, ϕ_{std} is the emission quantum yield of the standard (0.91 for fluoresceine with λ_{exc} = 470 nm[7]), A_{std} and A_s represent the absorbance of the standard and the sample at the excitation wavelength, while $\int I_{std}$ and $\int I_s$ are the integrals of the corrected emission envelopes of the standard and the sample respectively, and η is the refractive index of the solvents used for the samples and standards solutions.

$$\phi_s = \phi_{std}\left(\frac{A_{std}}{A_s}\right)\left(\frac{\int I_s}{\int I_{std}}\right)\left(\frac{\eta_s}{\eta_{std}}\right)^2$$

Table S2. *Photophysical data for **1**, **2**, and **3**, in methanol solution (1×10^{-6} mol L^{-1})*

Compound	λ_{abs} (log ε)	λ_{em}[a]	ϕ (%)[b]
3	328 (sh) ; 340 (4.45) ; 400 (sh) ; 458 (4.67) ; 480 (sh)	518 536	29
2	278 (4.84) ; 320 (4.46) ; 335 (4.46) ; 400 (sh) ; 448 (4.64) ; 472 (sh)	504 529	56
1	286 (5.00) ; 320 (sh) ; 335 (4.53) ; 400 (sh) ; 448 (4.75) ; 472 (sh)	503 524	67

[a] λ_{exc} = 450 nm for optimized emission intensity

[b] λ_{exc} = 470 nm and fluoresceine in NaOH 0.1 mol L^{-1} used as standard (ϕ = 0.91)

III-2 Experimental procedures

Typical procedures for fluorescence intensity quenching measurements

Stock solutions at 1×10^{-3} mol L^{-1} of **1**, **2**, and **3** were prepared in methanol. Samples for fluorescence measurements were prepared in 5 mL volumetric flasks with a constant concentration in **1** or **2** or **3** at 1×10^{-6} mol L^{-1} and with addition of increasing amount of picric acid (stock solutions at 1×10^{-3} mol L^{-1} and 1×10^{-2} mol L^{-1}). Completion of the volume was assured by methanol. Aliquots of 2 mL were placed in a quartz cell of 1 cm width. Their fluorescence spectra were recorded at 298K. Each measurement was repeated twice to get concordant value.

Fig. S4 *Fluorescence quenching for* ***2*** *(left) and* ***3*** *(right) (1×10^{-6} mol L^{-1}) upon addition of incremental amount of PA (1×10^{-3} mol L^{-1}) in methanol solution (excitation at 450 nm).*

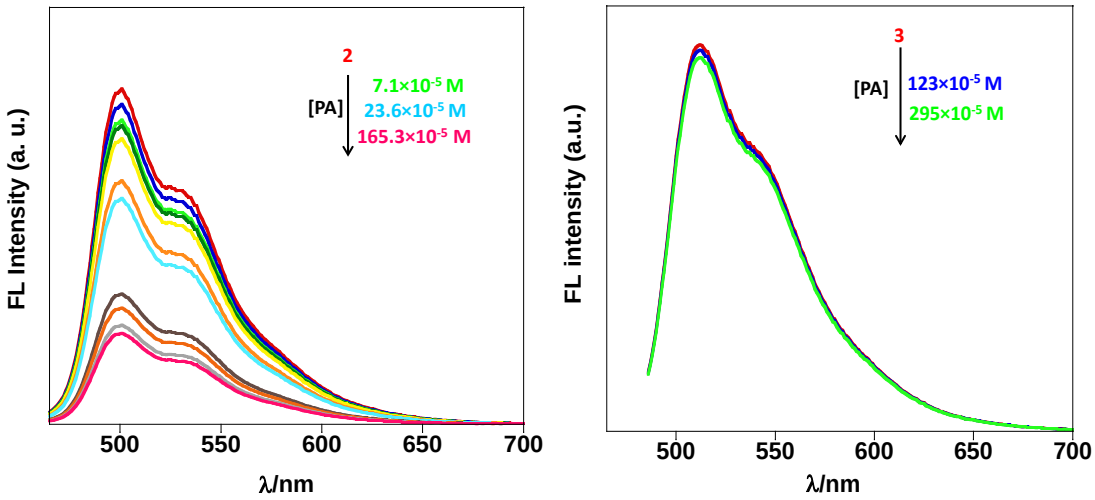
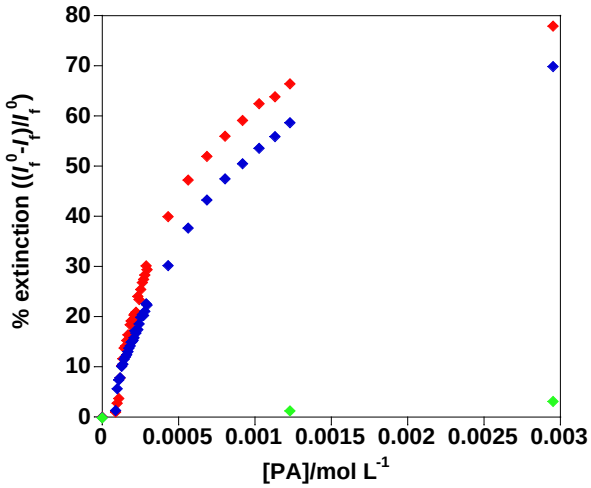


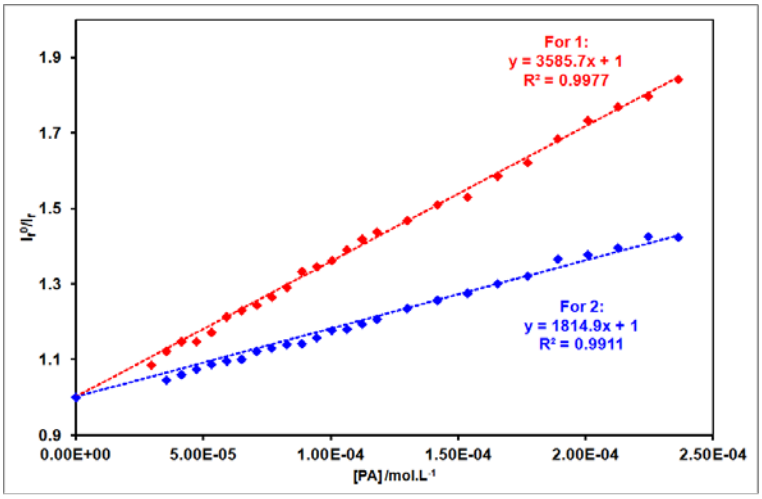
Fig. S5 *Percentage of fluorescence quenching ($(I_f^0 - I_f)/ I_f^0$) for* ***1*** *(red),* ***2*** *(blue), and* ***3*** *(green) as a function of [**PA**] (mol L^{-1}).*



Determination of the quenching constant K_{sv} by the Stern-Volmer method

The Stern-Volmer equation $\left(\frac{I_f^0}{I_f}\right) = 1 + Ksv \times [PA]$ is used to quantify the differences in quenching efficiency for the two probes **1** and **2**. In this equation, I_f^0 is the initial fluorescence intensity of the probe, without picric acid, I_f is the fluorescence intensity of the probe with an added fraction of picric acid, and K_{sv}, the Stern-Volmer constant, is the slope of the linear variation of $I_f°/I_f$ as a function of [PA].

Fig. S6 *Stern-Volmer plots for **1** (red) and **2** (blue) ($I_f^0/I_f = f([PA])$).*



Determination of the limit of detection (LOD) and limit of quantification (LOQ)

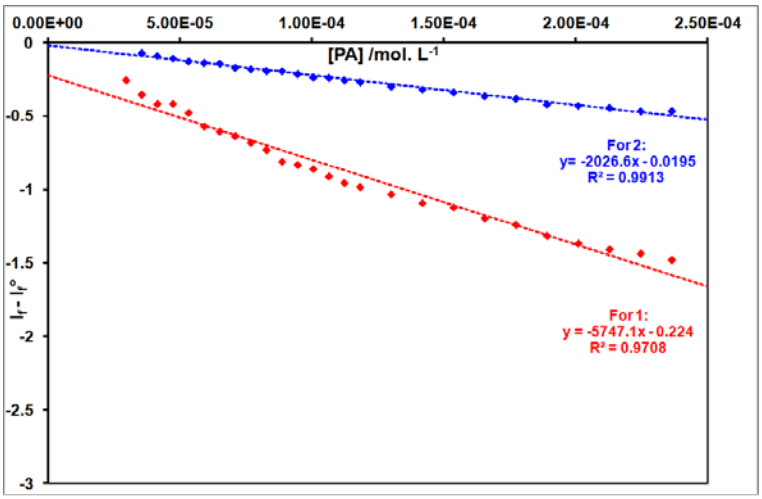
The calculation method for LOD and LOQ determination is based on the standard deviation of the response (SD) and the slope of the calibration curve (S) according to the formula: LOD = 3.3×(SD/S) and LOQ = 10×(SD/S). The standard deviation of the response can be determined based on the relation:

$SD = \sqrt{\frac{\sum(I_f^\circ - \bar{I_f^\circ})}{N-1}}$, with N = number of measures.

For **1**, the equation of the calibration curve is y = -5747.1x-0.224.
S = 5747.1 and SD = 0.0969 for N = 10
LOD = 5.52×10^{-5} mol L^{-1}
LOQ = 17.72×10^{-5} mol L^{-1}

For **2**, the equation of the calibration curve is y = -2026.6x-0.0195.
S = 2026.6 and SD = 0.1036 for N = 10
LOD = 16.87×10^{-5} mol L^{-1}
LOQ = 51.14×10^{-5} mol L^{-1}

Fig. S7 *Linear concentration range of PA (**1**: 1×10^{-6} mol L^{-1}; **2**: 1×10^{-6} mol L^{-1}) in methanol (excitation at 450 nm).*



Typical procedure for association constant K_a evaluation (Benesi-Hildebrand method)

Assuming a 1:1 stoichiometry, the equation $\frac{1}{I_f - I_f^0} = \frac{1}{Ka \times \Delta I_{fmax} \times [PA]} + \frac{[PA]}{\Delta I_{fmax}}$ was considered with

I_f = the fluorescence intensity of **1** or **2** in presence of picric acid

$I_f°$ = initial fluorescence intensity of **1** or **2**

ΔI_{fmax} = fluorescence intensity of free **1** compared to the fluorescence intensity of the 1/1 adduct

The curve $1/(I_f - I_f°)$ = f(1/[PA]) was plotted. The association constant was then obtained as the ratio between the intercept and the slope.

Fig. S8 *Benesi-Hildebrand plot (λ_{em} = 503 nm) for **1** (1×10^{-6} mol L^{-1}) assuming a 1:1 binding mode with excitation at 450 nm.*

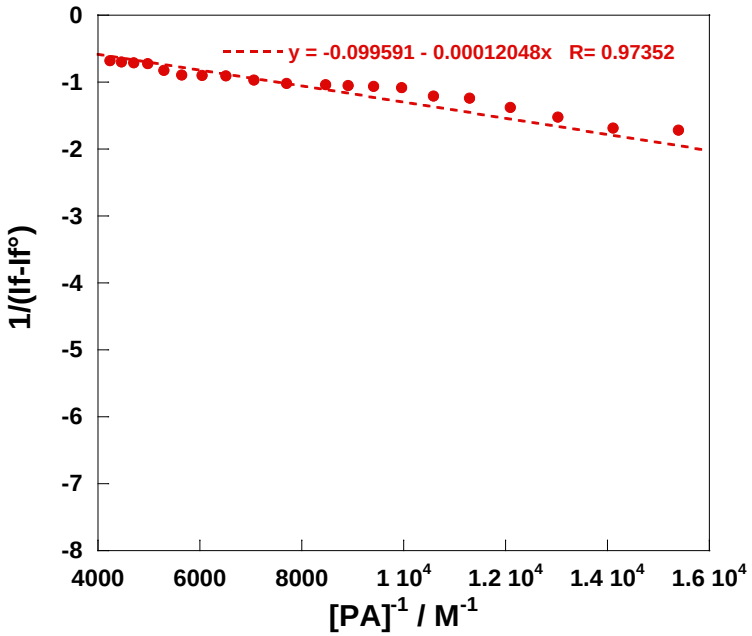
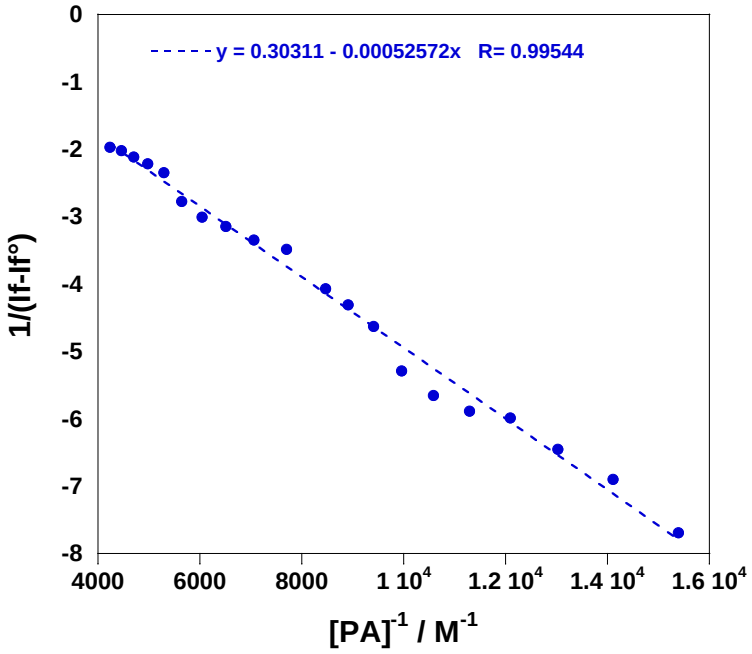


Fig. S9 *Benesi-Hildebrand plot (λ_{em} = 504 nm) for **2** (1×10^{-6} mol L^{-1}) assuming a 1:1 binding mode with excitation at 450 nm.*



Typical procedures for selectivity estimation

Samples were prepared as the same manner than previously mentioned from stock solutions in **1** or **2** at 1×10^{-3} mol L^{-1} and from stock solutions of the aromatic compounds at 1×10^{-2} mol L^{-1}. The final concentration in sensor was 1×10^{-6} mol L^{-1}, and 2.36×10^{-3} mol L^{-1} in aromatic compound (PA: picric acid; NP: 4-nitrophenol; NB: nitrobenzene; P: phenol; T: toluene; B: benzene). Aliquots of 2 mL were placed in a quartz cell of 1 cm width. Their fluorescence spectra were recorded at 298K. Each measurement was repeated twice to get concordant value.

Fig. S10 *Fluorescence quenching efficiency of **1** (red), **2** (blue), and **3** (green) upon addition of different aromatic compounds (excitation at 450 nm) (**PA**: picric acid; **NP**: 4-nitrophenol; **NB**: 4-nitrobenzene; **P**: phenol; **T**: toluene; **B**: benzene).*

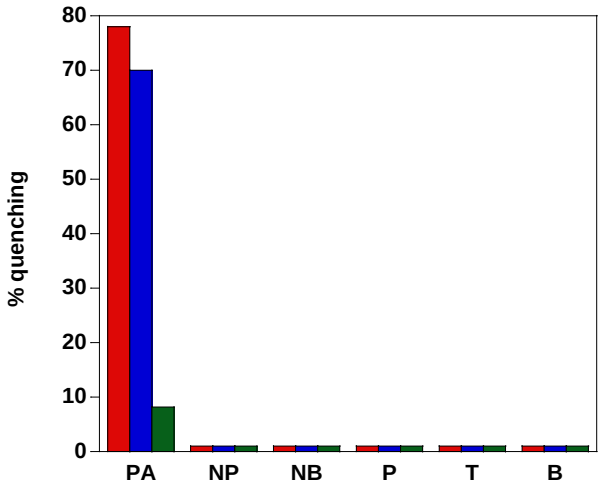
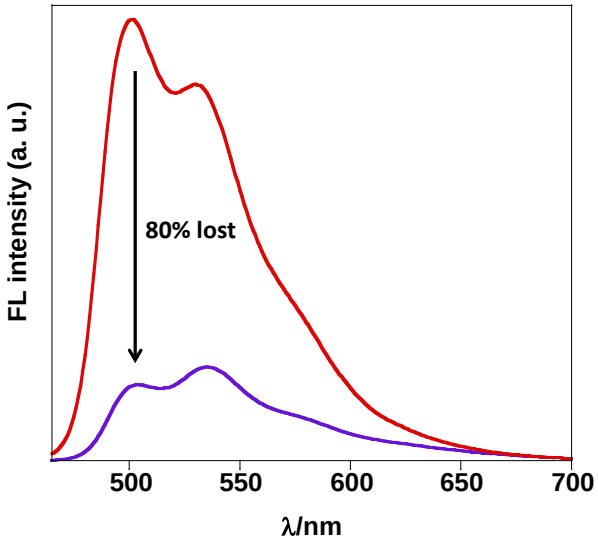


Fig. S11 *Emission spectra of* ***1*** *(red) and* ***1·PA*** *(violet) in methanol (7×10^{-6} mol L^{-1}; excitation at 450 nm).*



III-3 NMR measurements

Typical procedure for the continuous variation method (Job's method)

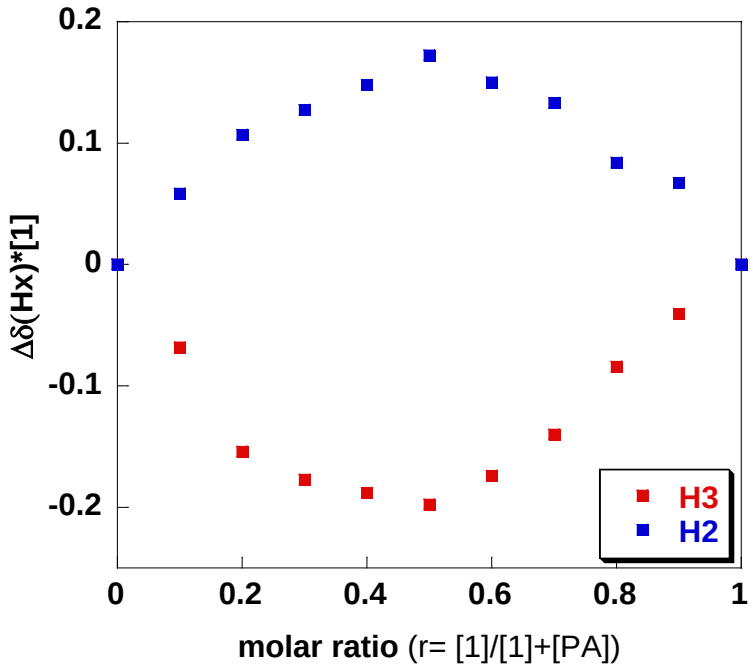
Samples were directly prepared in the NMR tubes by mixing aliquots of stock solution of **1** (5×10^{-3} mol L^{-1} in a mixture of 40% of DMSO-d_6 and 60% of CD_3OD) and stock solution of PA (5×10^{-3} mol L^{-1} in CD_3OD) in various proportions and with a total concentration of [**1**] + [PA] remaining constant and equals to 5×10^{-3} mol L^{-1} in each NMR tube. Volume of solvent in each NMR tube was also remained constant and equal de 0.5 mL. Chemical shifts of H2 and H3 were noted for each spectrum. The curve $(\delta_{obs}-\delta_{free}) \times$ [**1**] = f(r) was plotted with:

δ_{obs} = chemical shit of H2 or H3 in **1** when in interaction with PA

δ_{free} = chemical shit of H2 or H3 in **1** in its free form

r = the molar ratio equal to [1] / ([1] + [PA])

Fig. S12 *Job's plot for H2 (blue squares) and H32 (red squares) in **1** upon decreasing molar fraction of PA at a fixed concentration of 5×10^{-3} mol L^{-1}.*



Typical procedures for association constants Ka evaluation (Scott method)

Samples were directly prepared in the NMR tubes from stock solution of **1** or **2** (2.34×10^{-3} mol L^{-1} in a mixture of 40% of DMSO-d_6 and 60% of CD_3OD) and PA (5×10^{-3} mol L^{-1} in CD_3OD). Aliquots of stock solutions of **1** or **2** and PA were mixed in such a way as to maintain weak and constant the final concentration of **1** or **2** in the NMR tubes (0.5×10^{-3} mol L^{-1}). Concentration of PA in the NMR tubes was varied from 2×10^{-3} M to 12×10^{-3} M. The solvent volume in each NMR tube was maintained constant and was in consequence completed to 0.5 mL with CD_3OD. Chemical shifts of H2 and H3 were noted for each spectrum. The Scott equation was applied assuming a 1:1 stoichiometry

$\frac{[PA]}{\Delta\delta_{obs}} = \frac{[PA]}{\Delta\delta_{max}} + \frac{1}{Ka\times\Delta\delta_{max}}$ with

$\Delta\delta_{obs}$ = chemical shift variation for H3 in **1** or **2** when in interaction with PA, compared to the chemical shift of H3 in free **1** or **2**

$\Delta\delta_{max}$ = chemical shift variation for H3 in 1:1 adduct compared to H3 in free **1** or **2**

The curve [PA]/ $\Delta\delta_{obs}$ = f([PA]) was plotted. Slope of the obtained straight line was 1/ $\Delta\delta_{max}$, its intercept was 1/(Ka×$\Delta\delta_{max}$). The association constant was then obtained as the ratio between the slope and the intercept.

Fig. S13 *Scott's plot of the association between* ***1*** *and PA, as a function of [PA].*

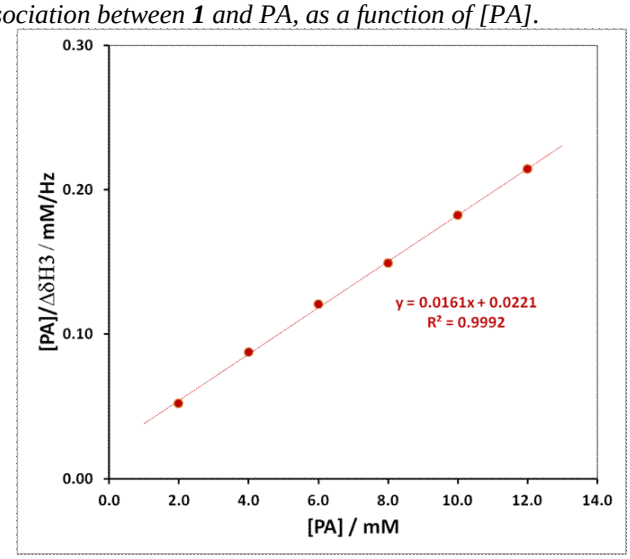


Fig. S14 *Scott's plot of the association between* ***2*** *and PA, as a function of [PA].*

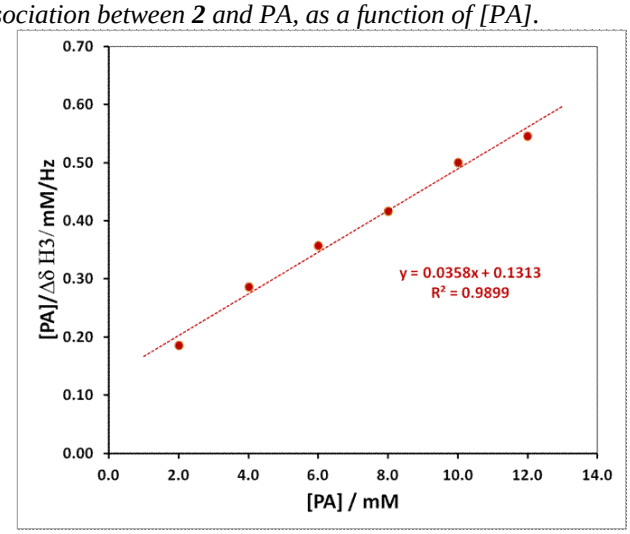
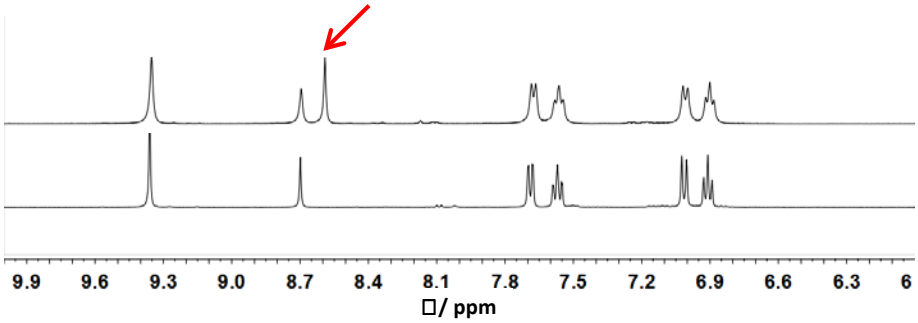


Fig. S15 *^{1}H NMR spectra of* ***3*** *(bottom) and* ***3*** *in presence of 2 equiv. of PA (top). The red arrow highlight the signal of PA.*



IV- Theoretical calculations

Computational Details

All the calculations described were carried out with the Gaussian 09 package.[8] The 6-31G(d) basis set was used for all calculations.[8,9] Molecular geometries of **1, 2** and **3** were optimized in a vacuum without symmetry restraint using DFT method with the B3LYP[8,10] hybrid exchange correlation functional implemented in the Gaussian suite of program. Optimizations were made from the X-Ray chemical structure for **1** and **3**, and after the adequate modification of the ester group from structure of **1**, for compound **2**. For all schemes the ground state minima have been confirmed by determination of the vibrational frequencies. Solvents effects on frontier orbitals energies were evaluated by means of the polarizable continuum model (PCM) in its integral equation formalism[11] and the default parameters were taken from the literature.[8] In the PCM model, the calculation was performed in the presence of a solvent (here MeOH) by placing the solute in a cavity within the solvent reaction field.

Fig. S16 *Caption Frontier orbitals energies diagram for 1, 2, and 3, and different aromatic compounds (PA: picric acid; NP: 4-nitrophenol; NB: 4-nitrobenzene; P: phenol; T: toluene; B: benzene).*

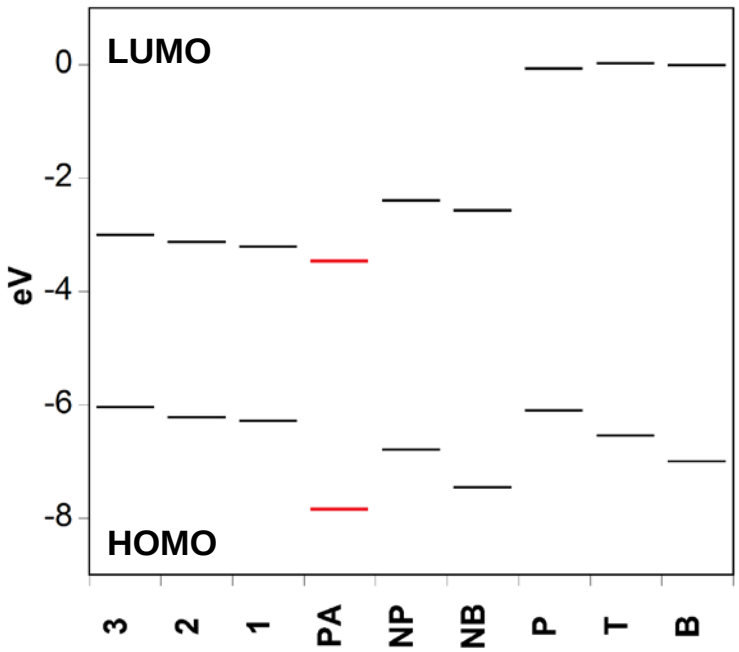


Table S3. *Frontier orbitals energies calculated for **1**, **2**, **3**, and the various aromatic compounds studied (**PA**: picric acid; **NP**: 4-nitrophenol; **NB**: 4-nitrobenzene; **P**: phenol; **T**: toluene; **B**: benzene)*

Compound	1	2	3	PA	NP	NB	P	T	B
LUMO (eV)	-3.221	-3.140	-3.013	-3.486	-2.413	-2.584	-0.081	+0.0104	-0.0203
HOMO (eV)	-6.266	-6.203	-6.017	-7.826	-6.772	-7.437	-6.074	-6.526	-6.981

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Table S4 Cartesian coordinates (Å) of the optimized geometry for **1**

Al	3.638797	0.964664	1.351098
N	-2.298863	-1.623694	-0.016159
N	-2.387235	0.598419	-1.358506
O	-4.714655	-2.395006	-1.070654
O	-4.632264	-0.223356	-2.684091
O	-5.843846	-7.255583	2.847603
O	-3.802588	-6.567449	3.601375
O	-6.395444	5.424159	-4.978756
O	-4.449660	5.980593	-3.924167
O	-2.654181	-1.915393	-2.853588
O	-4.764176	-0.025652	0.098406
C	-4.713953	-3.346637	-0.158427
C	-5.782757	-4.263905	-0.113521
C	-5.811472	-5.262671	0.841196
C	-4.774958	-5.404399	1.796002
C	-3.714210	-4.521201	1.767209
C	-3.652603	-3.482662	0.799546
C	-2.523483	-2.623558	0.812899
C	-1.117977	-0.853772	0.037575
C	-1.166962	0.360864	-0.693909
C	-0.049105	1.197789	-0.723335
C	-2.699136	1.771150	-1.872978
C	-3.860173	2.057975	-2.639749
C	-4.068828	3.397562	-3.067268
C	-5.148567	3.730173	-3.859982
C	-6.047965	2.710218	-4.258556
C	-5.868807	1.396293	-3.870804
C	-4.783363	1.033127	-3.047708
C	-4.893148	-6.513074	2.791142
C	-3.742379	-7.563669	4.599187
C	-2.696438	-8.476305	4.520287
C	-2.561463	-9.434271	5.526716
C	-3.466214	-9.468349	6.589181
C	-4.508511	-8.540420	6.648117
C	-4.653499	-7.575362	5.650753
C	-5.424470	5.123135	-4.327177
C	-4.553415	7.343458	-4.278185
C	-3.562682	7.865060	-5.102179
C	-3.593897	9.225860	-5.412717
C	-4.606101	10.039869	-4.901409
C	-5.590694	9.493343	-4.075080
C	-5.570002	8.135548	-3.754177
Al	-3.638797	-0.964664	-1.351098
H	-6.578342	-4.159621	-0.844029
H	-6.636810	-5.966805	0.881134
H	-2.913148	-4.622186	2.492893
H	-1.788961	-2.826638	1.593125
H	-0.087444	2.122242	-1.286063
H	-2.024712	2.611820	-1.703376
H	-3.367298	4.169522	-2.766224
H	-6.889724	2.993022	-4.883153
H	-6.557860	0.617925	-4.181785
H	-2.008367	-8.435398	3.681631
H	-1.752020	-10.156501	5.474638
H	-3.362042	-10.217342	7.368309
H	-5.215579	-8.566316	7.471839
H	-5.462080	-6.853501	5.684129
H	-6.331847	7.699460	-3.117109
H	-6.381274	10.123373	-3.678644
H	-4.630289	11.096931	-5.148144
H	-2.828983	9.645805	-6.059266
H	-2.788162	7.212758	-5.493358
H	-3.151426	-1.681156	-3.660889
H	-5.636506	-0.459060	0.134244
H	-4.927247	0.931918	0.045869
H	-2.667193	-2.887194	-2.796793
N	2.298863	1.623694	0.016159
N	2.387235	-0.598419	1.358506
O	4.714655	2.395006	1.070654
O	4.632264	0.223356	2.684091
O	5.843846	7.255583	-2.847603
O	3.802588	6.567449	-3.601375
O	6.395444	-5.424159	4.978756
O	4.449660	-5.980593	3.924167
C	4.713953	3.346637	0.158427
C	5.782757	4.263905	0.113521
C	5.811472	5.262671	-0.841196
C	4.774958	5.404399	-1.796002
C	3.714210	4.521201	-1.767209
C	3.652603	3.482662	-0.799546
C	2.523483	2.623558	-0.812899
C	1.117977	0.853772	-0.037575
C	1.166962	-0.360864	0.693909
C	0.049105	-1.197789	0.723335
C	2.699136	-1.771150	1.872978
C	3.860173	-2.057975	2.639749
C	4.068828	-3.397562	3.067268
C	5.148567	-3.730173	3.859982
C	6.047965	-2.710218	4.258556
C	5.868807	-1.396293	3.870804
C	4.783363	-1.033127	3.047708
C	4.893148	6.513074	-2.791142
C	3.742379	7.563669	-4.599187
C	2.696438	8.476305	-4.520287
C	2.561463	9.434271	-5.526716
C	3.466214	9.468349	-6.589181
C	4.508511	8.540420	-6.648117
C	4.653499	7.575362	-5.650753
C	5.424470	-5.123135	4.327177
C	4.553415	-7.343458	4.278185
C	3.562682	-7.865060	5.102179
C	3.593897	-9.225860	5.412717
C	4.606101	-10.039869	4.901409
C	5.590694	-9.493343	4.075080
C	5.570002	-8.135548	3.754177
H	6.578342	4.159621	0.844029
H	6.636810	5.966805	-0.881134
H	2.913148	4.622186	-2.492893

H	1.788961	2.826638	-1.593125
H	0.087444	-2.122242	1.286063
H	2.024712	-2.611820	1.703376
H	3.367298	-4.169522	2.766224
H	6.889724	-2.993022	4.883153
H	6.557860	-0.617925	4.181785
H	2.008367	8.435398	-3.681631
H	1.752020	10.156501	-5.474638
H	3.362042	10.217342	-7.368309
H	5.215579	8.566316	-7.471839
H	5.462080	6.853501	-5.684129
H	6.331847	-7.699460	3.117109
H	6.381274	-10.123373	3.678644
H	4.630289	-11.096931	5.148144
H	2.828983	-9.645805	6.059266
H	2.788162	-7.212758	5.493358
O	2.654181	1.915393	2.853588
O	4.764176	0.025652	-0.098406
H	3.151426	1.681156	3.660889
H	5.636506	0.459060	-0.134244
H	4.927247	-0.931918	-0.045869
H	2.667193	2.887194	2.796793

Table S5 Cartesian coordinates (Å) of the optimized geometry for **2**

Al	0.071439	3.980777	-0.684330
O	-1.238819	5.227615	-0.796458
O	-0.000082	3.630691	-2.686133
O	0.178115	4.473694	1.314625
O	7.504495	6.144022	0.305121
O	1.453030	5.096241	-1.090339
O	-7.301351	4.084315	0.775065
O	7.383133	3.948546	0.923116
N	-1.254381	2.516925	-0.347655
O	-7.336657	6.325529	0.337144
C	-3.194334	3.978712	-0.138157
C	2.719173	5.061896	-0.723523
C	-5.301668	5.185222	0.105904
N	1.339429	2.468227	-0.344953
C	-2.526402	2.728506	-0.077334
H	-3.140792	1.880378	0.227347
C	3.323912	3.870943	-0.190012
C	4.691849	3.893410	0.185429
H	5.166587	3.000845	0.584403
C	1.401511	-0.024760	-0.341342
H	2.480598	-0.041004	-0.435459
C	-2.528048	5.193981	-0.513925
C	-4.577581	4.011601	0.170941
H	-5.096399	3.102439	0.462802
C	5.454440	5.036073	0.053297
C	-1.401432	0.024422	-0.341287
H	-2.480505	0.040724	-0.435583
C	-0.689102	1.225662	-0.312656
C	6.894503	4.971583	0.480223
C	3.520439	6.212122	-0.863759
H	3.062425	7.106146	-1.274328
C	2.619163	2.641861	-0.084925
H	3.205310	1.783996	0.248318
C	0.728738	1.199156	-0.310516
C	-3.285401	6.379258	-0.580192
H	-2.779047	7.293764	-0.871736
C	-4.637194	6.373948	-0.278019
H	-5.206560	7.295433	-0.332194
C	8.944131	6.354346	0.648468
C	-6.764065	5.126185	0.446979
C	4.851189	6.199828	-0.481262
H	5.452742	7.095860	-0.588556
C	-8.786770	6.546323	0.621844
C	9.147070	6.126406	2.147782
H	8.469354	6.761103	2.728838
H	10.173673	6.397221	2.416264
H	8.982542	5.082896	2.421628
C	9.156706	7.821856	0.278312
H	8.958566	7.988875	-0.785269
H	10.192576	8.109413	0.483340
H	8.498444	8.471856	0.863651
C	9.810671	5.434320	-0.213657
H	9.646480	4.383583	0.030995
H	10.866105	5.669763	-0.040383
H	9.600872	5.592868	-1.276908
C	-9.072055	6.211610	2.087291
H	-8.943297	5.146551	2.287353
H	-10.105345	6.486412	2.324153
H	-8.411974	6.783657	2.748122
C	-9.628361	5.716123	-0.349541
H	-9.353052	5.939911	-1.385775
H	-10.684769	5.973723	-0.219274
H	-9.508479	4.646379	-0.170392
C	-8.948173	8.042559	0.354267
H	-8.304021	8.629822	1.016572
H	-9.985872	8.341041	0.532892
H	-8.695785	8.283577	-0.683372
Al	-0.071394	-3.981393	-0.683273
O	-1.452961	-5.097014	-1.088657
O	-0.177919	-4.473349	1.315865
O	0.000021	-3.631677	-2.684917
O	7.337075	-6.325555	0.336976
O	1.238761	-5.228318	-0.794616
O	-7.383567	-3.947852	0.922405
O	7.302065	-4.083954	0.773005
N	-1.339359	-2.468568	-0.344469
O	-7.505121	-6.143381	0.304667
C	-3.324037	-3.871060	-0.189653
C	2.528113	-5.194513	-0.512782
C	-5.454784	-5.035847	0.053377
N	1.254492	-2.517284	-0.347459
C	-2.619196	-2.642031	-0.084786
H	-3.205397	-1.784001	0.247965
C	3.194585	-3.978989	-0.138193

C	4.577997	-4.011668	0.170226
H	5.096963	-3.102303	0.461190
C	-2.719240	-5.062317	-0.722428
C	-4.692107	-3.893223	0.185318
H	-5.166882	-3.000451	0.583775
C	5.302033	-5.185337	0.105684
C	-0.728649	-1.199523	-0.310328
C	6.764586	-5.126071	0.446031
C	3.285424	-6.379859	-0.578560
H	2.778905	-7.294558	-0.869203
C	2.526657	-2.728781	-0.077679
H	3.141241	-1.880544	0.226256
C	0.689204	-1.226025	-0.312549
C	-3.520595	-6.212503	-0.862492
H	-3.062536	-7.106746	-1.272526
C	-4.851483	-6.199890	-0.480501
H	-5.453103	-7.095896	-0.587645
C	8.787274	-6.546217	0.621373
C	-6.894972	-4.971041	0.479818
C	4.637349	-6.374344	-0.277048
H	5.206688	-7.295869	-0.330819
C	-8.944887	-6.353415	0.647602
C	9.628535	-5.716985	-0.351114
H	9.352809	-5.941721	-1.387029
H	10.684983	-5.974496	-0.221022
H	9.508779	-4.647066	-0.172913
C	8.948435	-8.042714	0.355098
H	8.304534	-8.629308	1.018234
H	9.986190	-8.341119	0.533509
H	8.695550	-8.284667	-0.682201
C	9.073199	-6.210235	2.086403
H	8.944782	-5.144972	2.285558
H	10.106506	-6.485097	2.323107
H	8.413234	-6.781525	2.748000
C	-9.810982	-5.433349	-0.214923
H	-9.646662	-4.382616	0.029667
H	-10.866515	-5.668545	-0.041943
H	-9.600887	-5.592063	-1.278083
C	-9.148265	-6.125212	2.146808
H	-8.470789	-6.759882	2.728169
H	-10.174970	-6.395899	2.415009
H	-8.983718	-5.081679	2.420546
C	-9.157598	-7.820948	0.277604
H	-8.959092	-7.988179	-0.785872
H	-10.193596	-8.108273	0.482289
H	-8.499681	-8.470987	0.863285
H	-0.164222	5.380063	1.420614
H	1.037934	4.442443	1.768779
H	-0.856561	3.839327	-3.099237
H	0.646236	4.259756	-3.060989
H	-1.037274	-4.440745	1.770770
H	0.163528	-5.379998	1.422165
H	-0.644902	-4.261791	-3.060391
H	0.856939	-3.837665	-3.098419

Table S6 Cartesian coordinates (Å) of the optimized geometry for 3

Al	-3.986627	0.005603	-0.296092
C	-5.144486	2.629049	-0.122971
C	-6.319563	3.402541	-0.173322
C	-6.287987	4.752647	0.139139
C	-5.087648	5.394154	0.514205
C	-3.924133	4.660958	0.563132
C	-3.915722	3.272626	0.243666
C	-2.678255	2.581567	0.282058
C	-1.212510	0.714448	0.010460
C	-1.214230	-0.704118	0.029648
C	0.003633	1.400806	-0.017423
C	-2.695780	-2.557273	0.338283
C	-3.941183	-3.236243	0.272603
C	-3.994585	-4.598386	0.689562
C	-5.156691	-5.327170	0.584975
C	-6.307512	-4.712699	0.043235
C	-6.293100	-3.392312	-0.376511
C	-5.121486	-2.618143	-0.266275
N	-2.492782	1.305201	0.008533
N	-2.496011	-1.288613	0.041483
O	-5.202725	1.341113	-0.414962
O	-5.129261	-1.361325	-0.669197
O	-3.663174	0.046645	-2.303466
O	-4.463224	-0.067574	1.710561
H	-7.243686	2.910887	-0.459515
H	-7.208460	5.327951	0.095465
H	-5.086517	6.450974	0.757830
H	-2.987969	5.136635	0.845807
H	-1.812832	3.179900	0.570722
H	0.009414	2.483827	-0.026741
H	-1.844599	-3.153887	0.670958
H	-3.094189	-5.056553	1.092202
H	-5.191280	-6.362464	0.906285
H	-7.225373	-5.286880	-0.046114
H	-7.178089	-2.922553	-0.793216
H	-3.900817	0.896389	-2.715219
H	-5.358324	0.303251	1.816615
H	-4.462190	-0.929491	2.161905
H	-4.293029	-0.611955	-2.655273
C	5.144486	-2.629049	0.122971
C	6.319563	-3.402541	0.173321
C	6.287987	-4.752647	-0.139140
C	5.087648	-5.394154	-0.514206
C	3.924133	-4.660958	-0.563132
C	3.915722	-3.272626	-0.243666
C	2.678255	-2.581567	-0.282058
C	1.212510	-0.714448	-0.010460
C	1.214230	0.704118	-0.029648
C	-0.003633	-1.400806	0.017423
C	2.695780	2.557273	-0.338283
C	3.941183	3.236243	-0.272603
C	3.994585	4.598386	-0.689561

C	5.156691	5.327170	-0.584974
C	6.307512	4.712699	-0.043234
C	6.293100	3.392312	0.376511
C	5.121486	2.618143	0.266275
N	2.492782	-1.305201	-0.008533
N	2.496011	1.288613	-0.041483
O	5.202725	-1.341113	0.414962
O	5.129261	1.361325	0.669197
H	7.243686	-2.910887	0.459515
H	7.208460	-5.327951	-0.095465
H	5.086517	-6.450974	-0.757831
H	2.987969	-5.136635	-0.845807
H	1.812832	-3.179900	-0.570722
H	-0.009414	-2.483827	0.026741
H	1.844599	3.153887	-0.670958
H	3.094189	5.056553	-1.092202
H	5.191280	6.362464	-0.906284
H	7.225373	5.286880	0.046114
H	7.178089	2.922553	0.793217
Al	3.986627	-0.005603	0.296092
O	3.663174	-0.046645	2.303466
O	4.463224	0.067574	-1.710561
H	3.900817	-0.896389	2.715219
H	5.358324	-0.303251	-1.816615
H	4.462190	0.929491	-2.161904
H	4.293029	0.611954	2.655273