Protonation-induced Chromism of Pyridylethynyl-appended [core+*exo*]-type Au₈ Clusters. Resonance-coupled Electronic Perturbation through π-Conjugated Group.

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I. Experimental

A. Materials

Tetrachloroauric(III) acid tetrahydrate (>47.5% for gold) were obtained from Kojima Chemicals. 1,3-bis(diphenylphosphino)propane (dppp, 97%) and sodium borohydride (99%) were obtained from Aldrich. Phenylacetylene (98%), 1-hexyne (97%), 2-ethynylpyridine (95%), 3-ethynylpyridine (98%), 4-ethynylpyridine (98%) and methanesulfonic acid (99%) were obtained from TCI. Methanol-d4 was obtained from Euriso-top. Sodium methoxide (95%), 2-aminoethanol (99%) and concentrated hydrochloric acid (35-37%) were purchased from Wako Pure Chemical Industries. Methanol (99.5%), dichloromethane (99%) and ether (99%) were obtained from Kanto Chemicals. All the above reagents were used as received.   [Au₈(dppp)₄](NO₃)₂ (**1**·(NO₂)₂) was prepared by four steps from tetrachloroauric acid according to procedures reported previously.[1]

B. Measurements

UV-visible absorption spectra were recorded using a JASCO V-670 double-beam spectrometer at 25 °C. Photoluminescence and excitation spectra were recorded on a JASCO FP-6500 spectrofluorometer equipped with a Hamamatsu Photonics R928 photomultiplier tube detector. Electrospray ionization mass (ESI-MS) spectra were recorded on a Bruker micrOTOF-HS. ¹H and proton-decoupled ³¹P NMR spectra were collected in CD₃OD at ambient temperature on a JEOL EX-400 NMR spectrometer, and the chemical shifts (in ppm) were referenced to residual $CH_nD_{3-n}OD$ (δ = 3.30) and 85% H_3PO_4 (external standard, δ = 0.00), respectively. Single crystal data was collected on a Bruker SMART Apex II CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The crystal structure was solved by direct methods (SHELXS-97)[1] and refined by full-matrix least-squares methods on F^2 (SHELXL-97)[2] with APEX II software. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at calculated positions and refined isotropically.

C. Synthesis

[Au₈(dppp)₄(C≡CPh)₂](NO₃)₂ **2**·(NO₃)₂: To a methanolic solution (50 mL) of **1**·(NO₂)₂ (30.0 mg, 9 μmol) was added phenylacetylene (2.0 μL, 18 μmol) and sodium methoxide (145 mg, 2.7 mmol), and the mixture was stirred at room temperature under air and room light. After 10 h, the mixture was treated with water and then extracted with dichloromethane (20 mL × 3). The combined organic phase was dried over anhydrous Na₂SO₄, filtered and evaporated to dryness to give a pinkish solid, which was further purified by vapor diffusion of ether into a cluster solution in dichloromethane/methanol (~50/50 v/v) to give **2**·(NO₃)₂ as red crystals (15.7 mg, 45%). Elemental analysis: calcd (%) for **2**·(NO₃)₂(CH₂Cl₂)₄ (C₁₂₈H₁₂₂N₂O₆P₈Au₈Cl₈): C 39.51, H 3.16, N 0.72; found: C 39.66, H 3.27, N 0.55.

ESI-MS: 1713.15 ($[M-2NO_3]^{2+}$). ^{1}H-NMR: δ1.39 (br, 4H), 2.15 (br, 4H), 2.37 (br, 4H), 2.63-2.73 (br, 12H), 6.59 (t, 8H), 6.66 (m, 12H), 6.75 (d, 4H), 6.87-7.04 (m, 18H), 7.13 (t, 4H), 7.33 (t, 8H), 7.42 (d, 12H), 7.53-7.57 (m, 8H), 7.89-7.94 (m, 8H), 8.21 (br, 8H). ^{31}P-NMR: δ 38.83 (2P), 51.43 (4P), 55.62 (2P).

3·(NO$_3$)$_2$, **- 6**·(NO$_3$)$_2$ were prepared in similar manners to the above.

3·(NO$_3$)$_2$: (20% after recrystallization by vapor diffusion of ether into a cluster solution in dichloromethane/methanol (~50/50 v/v)). Elemental analysis: calcd (%) for **3**·(NO$_3$)$_2$(H$_2$O)$_2$ (C$_{120}$H$_{126}$N$_2$O$_8$P$_8$Au$_8$): C 40.63, H 3.58, N 0.79; found: C 40.55, H 3.53, N 0.65. ESI-MS: 1693.2 ($[M-2NO_3]^{2+}$). ^{1}H-NMR: δ0.66 (t, 6H), 1.28 (br, 8H), 1.60-1.69 (br, 8H), 2.06 (br, 4H), 2.24 (br, 4H), 2.46 (br, 4H), 2.62-2.71 (br, 8H), 6.66 (t, 8H), 6.83 (t, 8H), 6.97-7.20 (m, 20H), 7.42-7.55 (m, 28H), 7.90 (m, 8H), 8.13 (br, 8H). ^{31}P-NMR: δ 38.45 (2P), 50.78 (4P), 55.73 (2P).

4·(NO$_3$)$_2$: (35% after recrystallization from methanol/ether). Elemental analysis: calcd (%) for **4**·(NO$_3$)$_2$ (C$_{122}$H$_{112}$N$_4$O$_6$P$_8$Au$_8$): C 41.23, H 3.18, N 1.58; found: C 41.42, H 3.38, N 1.33. ESI-MS: 1714.14 ($[M-2NO_3]^{2+}$). ^{1}H-NMR: δ1.43 (br, 4H), 2.19 (br, 4H), 2.39 (br, 4H), 2.69-2.77 (br, 12H), 5.94 (d, 2H), 6.60 (t, 8H), 6.73 (t, 8H), 6.92-7.05 (m, 16H), 7.15 (t, 4H), 7.33 (t, 8H), 7.43 (m, 12H), 7.52-7.57 (m, 12H), 7.97 (m, 8H), 8.15 (br, 8H), 8.26 (d, 2H). ^{31}P-NMR: δ 38.59(2P), 51.82 (4P), 55.71 (2P).

5·(NO$_3$)$_2$: (33% after recrystallization methanol/ether). Elemental analysis: calcd (%) for **5**·(NO$_3$)$_2$(H$_2$O)$_2$ (C$_{122}$H$_{116}$N$_4$O$_8$P$_8$Au$_8$): C 40.82, H 3.26, N 1.56; found: C 40.77, H 3.26, N 1.51. ESI-MS: 1714.14 ($[M-2NO_3]^{2+}$). ^{1}H-NMR: δ1.52 (br, 4H), 2.19 (br, 4H), 2.38 (br, 4H), 2.67-2.76 (br, 12H), 6.51-6.54 (m, 2H), 6.61 (t, 8H), 6.67 (t, 8H), 6.95-7.07 (m, 16H), 7.16 (t, 4H), 7.32-7.37 (m, 8H), 7.42 (br, 8H), 7.47-7.58 (m, 16H), 7.94 (m, 8H), 8.03 (d, 2H), 8.17 (br, 8H). ^{31}P-NMR: δ 38.51 (2P), 51.38 (4P), 55.77 (2P).

6·(NO$_3$)$_2$: (48% after recrystallization methanol/ether). Elemental analysis: calcd (%) for **6**·(NO$_3$)$_2$(H$_2$O)$_3$ (C$_{122}$H$_{118}$N$_4$O$_9$P$_8$Au$_8$): C 40.62, H 3.30, N 1.55; found: C 40.7, H 3.28, N 1.36. ESI-MS: 1714.18 ($[M-2NO_3]^{2+}$). ^{1}H-NMR: δ1.49 (br, 4H), 2.17 (br, 4H), 2.38 (br, 4H), 2.69-2.78 (br, 12H), 6.57-6.62 (m, 12H), 6.70 (t, 8H), 6.95-7.06 (m, 16H), 7.15 (t, 4H), 7.35-7.41 (br, 16H), 7.50-7.57 (m, 12H), 7.74 (d, 4H), 7.96 (m, 8H), 8.15 (br, 8H). ^{31}P-NMR: δ 38.57 (2P), 51.49 (4P), 55.98 (2P).

ESI-MS and ^{31}P NMR spectra of **2**·(NO$_3$)$_2$ - **6**·(NO$_3$)$_2$ are provided in Figures S1 and S2, respectively.
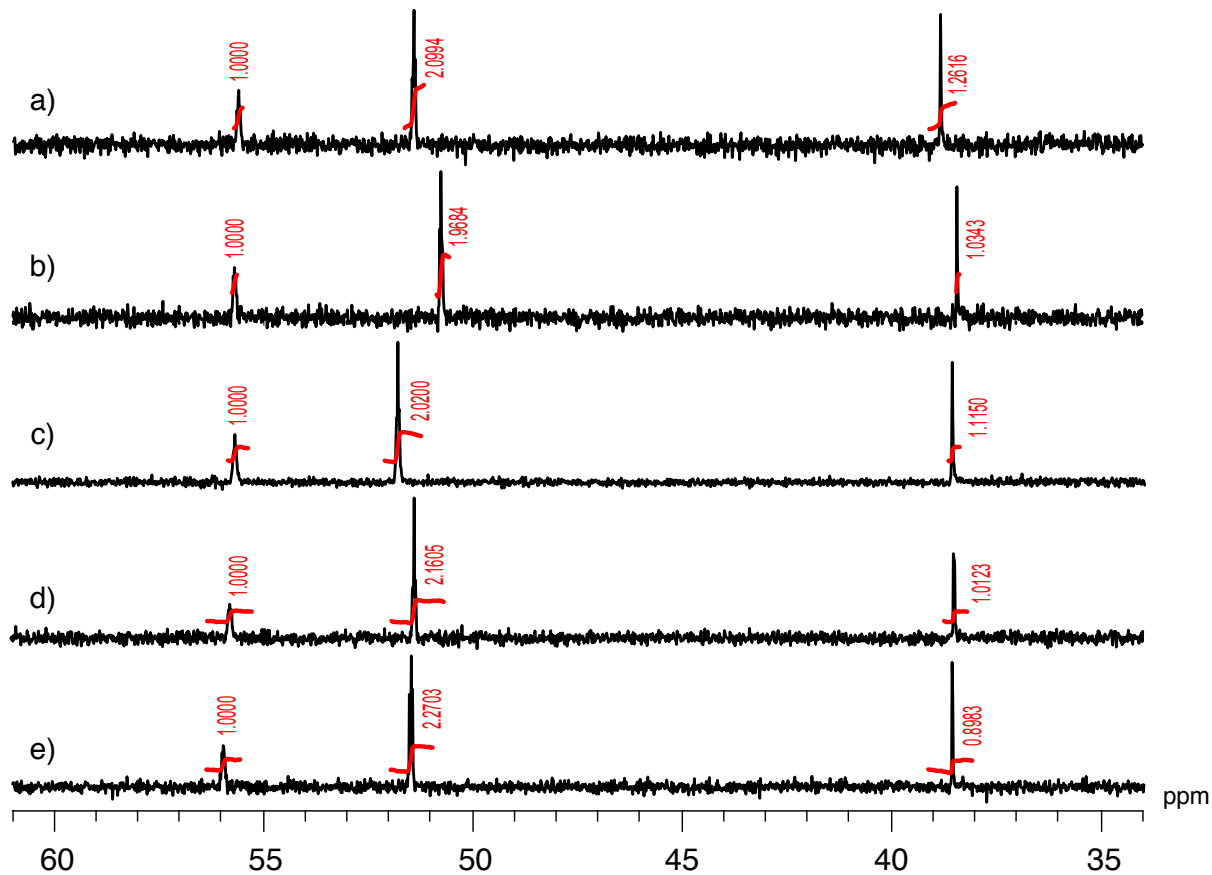
II. Results

A. ESI mass spectra
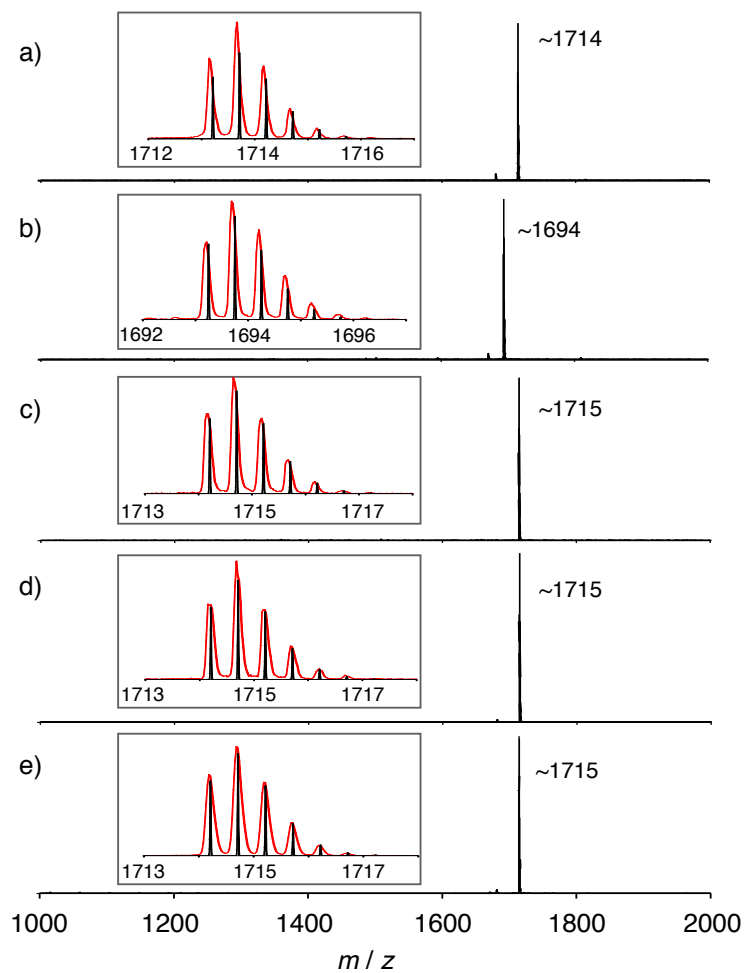
Figure S1 Positive-ion ESI mass spectra of nitrate salts of a) **2**, b) **3**, c) **4**, d) **5** and e) **6** in MeOH. The insets show the comparison of the experimental data (red lines) with the calculated isotope patterns for the divalent cluster cations (black bars).

B. ^{31}P NMR spectra

Figure S2. Proton-decoupled ^{31}P NMR spectra of nitrate salts of a) **2**, b) **3**, c) **4**, d) **5** and e) **6** in CD$_3$OD at room temperature.

C. Crystal data of 2·(NO$_3$)$_2$

**Table S1.** Crystal data and structure refinement for 2·(NO$_3$)$_2$.

|	
Empirical formula	C$_{126}$H$_{122}$Au$_8$N$_2$O$_8$P$_8$
Formula weight	3615.75
Temperature	90 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*C2/c*
Unit cell dimensions	$a = 31.2188(14)$ Å $\quad \alpha = 90°$
	$b = 17.1001(7)$ Å $\quad \beta = 90.3710(10)°$
	$c = 23.3745(10)$ Å $\quad \gamma = 90°$
Volume	12478(9) Å^3
Z	4
Density (calculated)	1.925 Mg/m^3
Absorption coefficient	9.524 mm^{-1}
F(000)	6832
Crystal size	0.24 x 0.29 x 0.31 mm^3
Theta range for data collection	1.30 to 26.73°
Index ranges	$-39 \leq h \leq 31, -13 \leq k \leq 21, -29 \leq l \leq 29$
Reflections collected	33205
Independent reflections	13230 [R(int) = 0.0342]
Reflections with $I > 2\sigma(I)$	10895
Completeness to theta = 26.73°	99.7 %
Absorption correction	Empirical
Max. and min. transmission	0.2083 and 0.1562
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13230 / 3 / 657
Goodness-of-fit on F^2	1.125
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0347, wR_2 = 0.1054$
R indices (all data)	$R_1 = 0.0489, wR_2 = 0.1219$
Largest diff. peak and hole	4.643 and -2.855 eÅ^{-3}

D. ORTEP drawing of 2·(NO₃)₂.
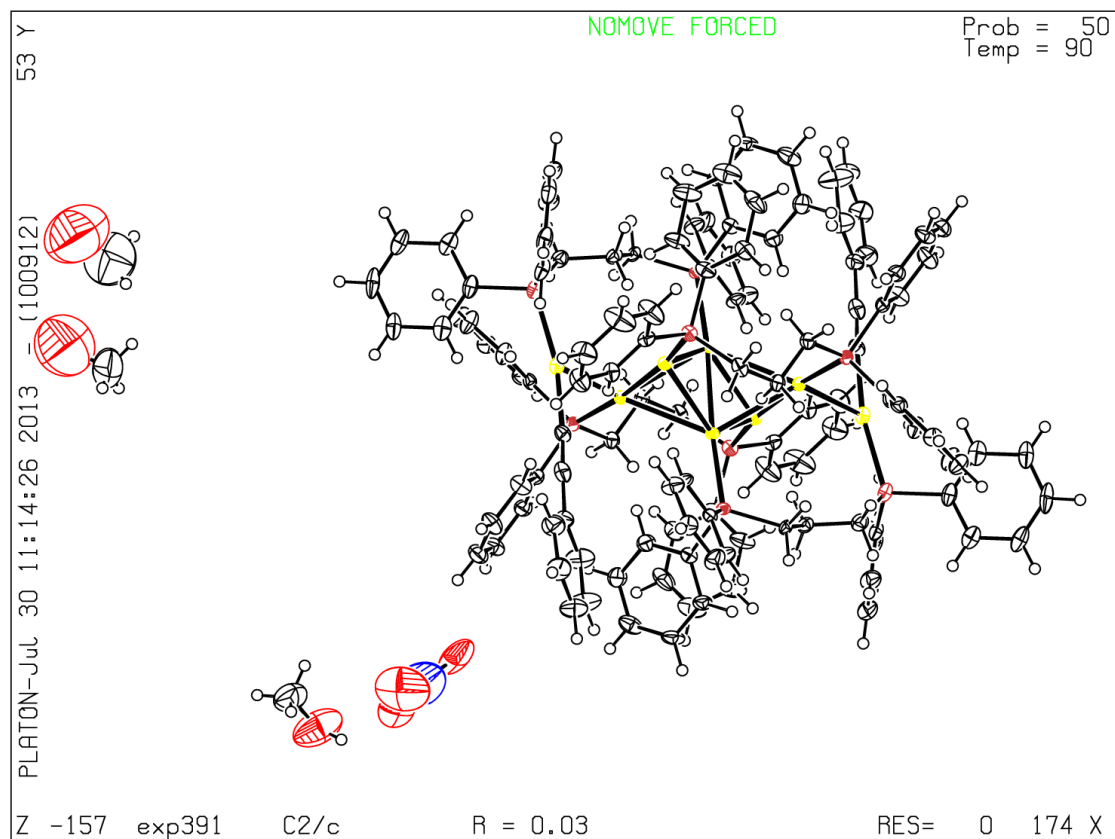
Figure S3. ORTEP drawing of **2**·(NO₃)₂. Thermal ellipsoids are drawn at the 50% probability level. For clarity, hydrogen atoms are omitted.

E. Spectroscopic titration experiments.
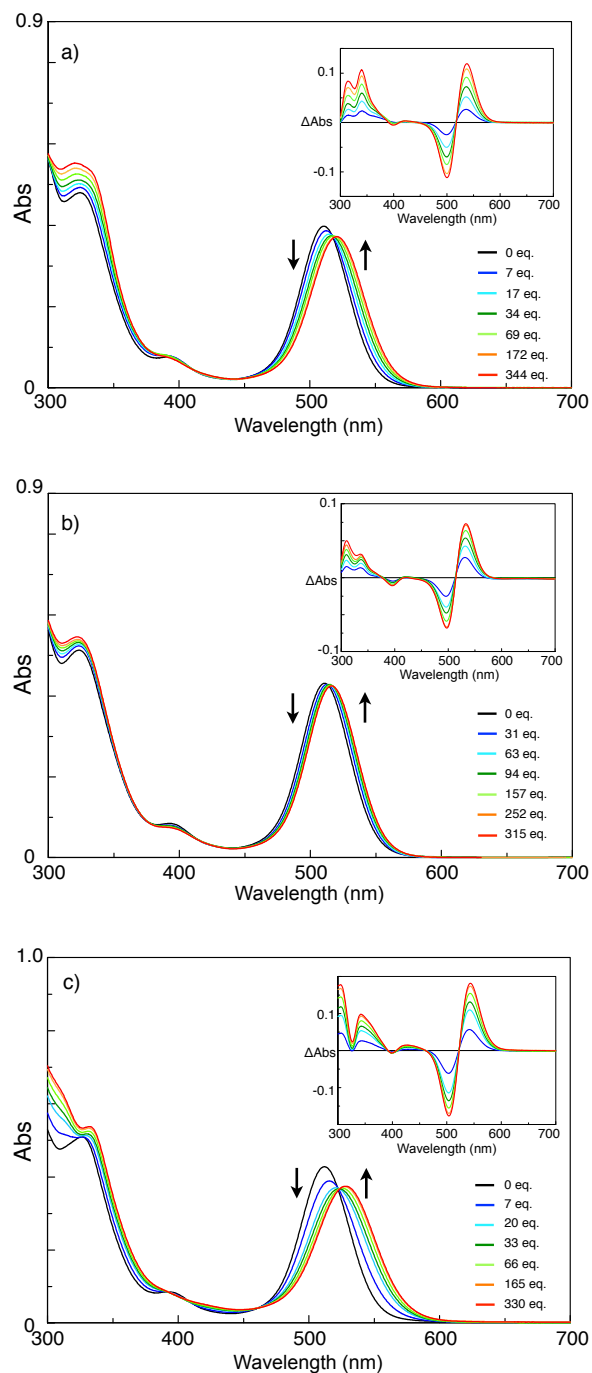
Figure S4. Absorption spectral changes of a) **4** (9.7 μM), b) **5** (10.6 μM) and c) **6** (10.1μM) in MeOH upon titration with aq. HCl. The insets show subtracted spectra. The host cluster solutions were prepared by dissolving weighed crystals (∼ 2 mg) of the nitrate salts of **4** - **6** in MeOH (50 mL). A 3 mL portion of the cluster solution was titrated with 100 mM acid solution (aq. HCl, aq. HBF_4, or methanolic $MeSO_3H$) in a 10-mm quartz cell and the spectral changes were monitored by UV-visible absorption spectroscopy at 25 °C.
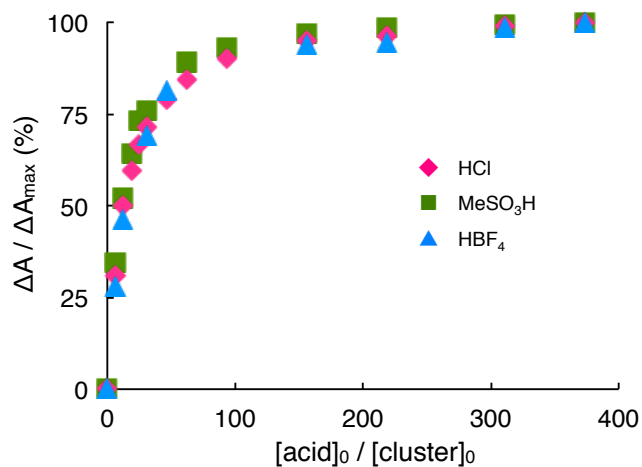
Figure S5. Spectrophotometric titration (monitoring wavelength: 543 nm) of **6** in MeOH (10.7 μM) with aq. HCl, aq. HBF$_4$, and methanolic MeSO$_3$H at 25 °C.
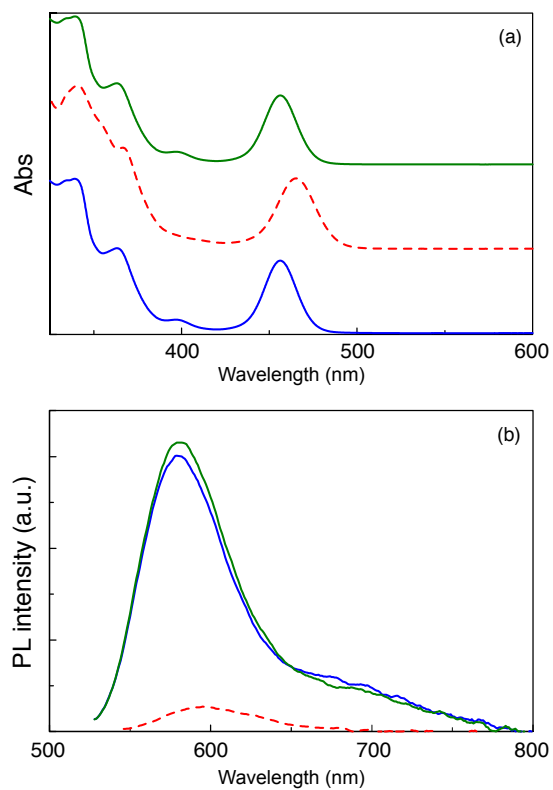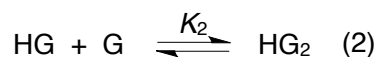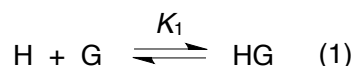

Figure S6. Absorption (a) and photoluminescence (λ_{ex} = 510 nm) (b) spectra of **6** in MeOH (10.1μM) before (blue) and after (red) the addition of aqueous HCl (370 eq), and after neutralization of the acidified sample by the addition of 2-aminoethanol (370 eq) (green).

F. Determination of binding constants.

The binding affinities of **4** - **6** towards HCl were estimated from the absorbance changes at 537, 533, and 543 nm, respectively, since they were found observed to be the maxima in the subtracted spectra. Since the host clusters (H) have two pyridyl moieties, the interaction with HCl (G) should involve two equilibrium processes (eqn (1) and (2)). Based on the reported protocol utilizing Origin software,[2] the observed binding isotherms (Figure 3) were fitted to the 1:2 host-guest binding system to give K_1 and K_2 together with the absorption molar absorptivity of free (ε_0), monoprotonated (ε_1) and diprotonated (ε_2) species at the monitoring wavelength.

$$H + G \xrightleftharpoons{K_1} HG \quad (1)$$

$$HG + G \xrightleftharpoons{K_2} HG_2 \quad (2)$$

$$(H = [Au_8(C{\equiv}CPy)_2]^{2+}, G = H^+)$$

$$Abs_{obs} = \frac{[H]_t \times (\varepsilon_0 + \varepsilon_1 K_1[G]_t + \varepsilon_2 K_1 K_2([G]_t)^2)}{1 + K_1[G]_t + K_1 K_2([G]_t)^2}$$

Table S2. Results of non-linear curve fitting of the spectrophotometric titration data of **4** – **6** with HCl.

cluster	$\lambda_{mon.}$ (nm)	K_1 (M^{-1})	K_2 (M^{-1})	ε_0 (M^{-1} cm^{-1})	ε_1 (M^{-1} cm^{-1})	ε_2 (M^{-1} cm^{-1})	R^2	χ^2
4	537	5.9×10^3	9.5×10^2	1.6×10^4	2.5×10^4	2.9×10^4	0.99943	8.96E^{-7}
5	533	1.3×10^3	5.0×10^2	2.1×10^4	2.8×10^4	2.8×10^4	0.99971	1.54E^{-7}
6	543	1.2×10^4	1.6×10^3	1.1×10^4	2.4×10^4	2.8×10^4	0.99996	1.03E^{-7}

References

(1)   Kamei, Y.; Shichibu, Y.; Konishi, K., *Angew. Chem. Int. Ed.* **2011**, *50*, 7442-7445.

(2)   Hargrove, A.; Zhong, Z.; Sessler, J.; Anslyn, E., *New. J. Chem.* **2010**, *34*, 348-354.