Oxaazamacrocycles incorporating quinoline moiety: synthesis and study of their binding properties towards metal cations

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Supporting information

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1. Studies of binding metal ions by 5a

1.1 Fluorimetric and UV-vis studies of binding metal ions by 5a

**Figure S1.** Fluorescence spectra of 5a ([5a] = 26 μM) in CH$_3$CN before and after addition of 4 equiv. of metal perchlorates in CH$_3$CN ($\lambda_{ex}$ = 397 nm).

**Figure S2.** UV-vis spectra of 5a ([5a] = 26 μM) in CH$_3$CN before and after addition of 4 equiv. of metal perchlorates in CH$_3$CN.
1.2 Fluorimetric and spectrophotometric titrations of 5a with Cu$^{2+}$ ions

**Figure S3.** Evolution of fluorescence spectrum of 5a (26 μM solution in CH$_3$CN) upon addition of Cu(ClO$_4$)$_2$ (0 - 2.2 equiv.) ($\lambda_{ex} = 397$ nm).

**Figure S4.** (a) Changes of emission intensities at 488 nm plotted against [Cu(ClO$_4$)$_2$]/[5a]$_{tot}$. (b) Job’s plot derived from the titration curve$^2$.

Stability constants calculated using SPECFIT$^1$

$\lg(\beta_{Cu(5a)2}) = 11.7\pm0.5$ , $\lg(\beta_{Cu(5a)}) = 7.0\pm0.5$
**Figure S5.** (a) Evolution of UV–vis spectrum of 5a (394 μM solution in CH$_3$CN) upon addition of Cu(ClO$_4$)$_2$ (0 - 1.3 equiv.). (b) UV-vis spectra of 5a (red), [Cu(5a)$_2$]$^{2+}$ (green) and [Cu(5a)]$^{2+}$ (magenta) calculated using SPECFIT$^1$. (c) Species distribution diagram for the Cu$^{2+}$/5a system in CH$_3$CN calculated using SPECFIT$^1$.

**Figure S6.** (a) Changes of absorbance at 395 nm plotted against [Cu(ClO$_4$)$_2$]/[5a]$_{tot}$. (b) Job’s plot derived from the titration curve$^2$.

Stability constants calculated using SPECFIT$^1$

$\lg(\beta_{\text{Cu}(5a)_2}) = 10.5\pm0.3$, $\lg(\beta_{\text{Cu}(5a)}) = 6.3\pm0.3$
1.3 Fluorimetric and spectrophotometric titrations of 5a with Al$^{3+}$ ions

![Graph showing the evolution of fluorescence spectrum of 5a](image)

**Figure S7.** Evolution of fluorescence spectrum of 5a (26 μM solution in CH$_3$CN) upon addition of Al(ClO$_4$)$_3$ (0 - 1.2 equiv.) ($\lambda_{ex} = 397$ nm).

![Graph showing changes of emission intensities at 488 nm](image)

**Figure S8.** (a) Changes of emission intensities at 488 nm plotted against [Al(ClO$_4$)$_3$]/[5a]$_{tot}$. (b) Job’s plot derived from the titration curve.

Stability constants calculated using SPECFIT

$\log(\beta_{Al(5a)2}) = 11.85 \pm 0.05$
Figure S9. (a) Evolution of UV–vis spectrum of 5a (26 μM solution in CH$_3$CN) upon addition of Al(ClO$_4$)$_3$ (0 - 1.1 equiv.); (b) Normalized UV-vis spectra of 5a (red) and [Al(5a)$_2$]$^{3+}$ (green) calculated using SPECFIT$^1$. (c) Species distribution diagram for the Al$^{3+}$/5a system in CH$_3$CN calculated using SPECFIT$^1$

Figure S10. (a) Changes of absorbance at 395 nm plotted against [Al(ClO$_4$)$_3$]/[5a]$_{tot}$. (b) Job’s plot derived from the titration curve$^2$. Stability constants calculated using SPECFIT$^1$

$\log(\beta_{Al(5a)2}) = 11.15 \pm 0.07$
2. Studies of binding metal ions by 5b

2.1 Fluorimetric and UV-vis studies of binding metal ions by 5b

![Fluorescence spectra of 5b](image1)

**Figure S11.** Fluorescence spectra of 5b ([5b] = 24 μM) in CH₃CN before and after addition of 4 equiv. of metal perchlorates in CH₃CN (λₑₓ = 395 nm).

![UV-vis spectra of 5b](image2)

**Figure S12.** UV-vis spectra of 5b ([5b] = 24 μM) in CH₃CN before and after addition of 4 equiv. of metal perchlorates in CH₃CN.
3. Studies of binding metal ions by 5c

3.1 Fluorimetric and UV-vis studies of binding metal ions by 5c

Figure S13. Fluorescence spectra of 5c ([5c] = 24 μM) in CH$_3$CN before and after addition of 4 equiv. of metal perchlorates in CH$_3$CN ($\lambda_{ex} = 385$ nm).

Figure S14. UV-vis spectra of 5c ([5c] = 24 μM) in CH$_3$CN before and after addition of 4 equiv. of metal perchlorates in CH$_3$CN.

Figure S15. Absorbance of 5c (24 μM solution in CH$_3$CN) in the presence of different metal ions (4 equiv.) at different wavelengths: (a) 390 nm, (b) 288 nm.
Figure S16. Cross-selectivity studies of metal ion binding by ligand 5c (24 μM solution in CH$_3$CN, $\lambda_{ex} = 385$ nm) using fluorescence spectroscopy:

(S_1) emission spectrum of 5c,

(S_2) emission spectrum of 5c after addition of Cu$^{2+}$ (1 equiv.),

(S_3) emission spectrum of 5c after addition of Li$^+$, Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Ba$^{2+}$ (1 equiv. of each metal ion),

(S_4) emission spectrum of 5c after addition of Li$^+$, Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Ba$^{2+}$ (1 equiv. of each metal ion) and Cu$^{2+}$ (1 equiv.)

(S_5) emission spectrum of 5c after addition of Fe$^{2+}$, Mn$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Zn$^{2+}$ (1 equiv. of each metal ion),

(S_6) emission spectrum of 5c after addition of Fe$^{2+}$, Mn$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Zn$^{2+}$ (1 equiv. of each metal ion) and Cu$^{2+}$ (1 equiv.)

(S_7) emission spectrum of 5c after addition of Al$^{3+}$ (1 equiv.),

(S_8) emission spectrum of 5c after addition of Al$^{3+}$ (1 equiv) and Cu$^{2+}$ (1 equiv.)

(S_9) emission spectrum of 5c after addition of Ag$^{2+}$, Hg$^{2+}$, Cd$^{2+}$, Pb$^{2+}$ (1 equiv. of each metal ion),

(S_10) emission spectrum of 5c after addition of Ag$^{2+}$, Hg$^{2+}$, Cd$^{2+}$, Pb$^{2+}$ (1 equiv. of each metal ion) and Cu$^{2+}$ (1 equiv.)
Figure S17. Cross-selectivity studies of metal ion binding by ligand 5c (24 μM solution in CH₃CN, λₑₓ = 385 nm) using UV-vis spectroscopy:

(S_1) UV-vis spectrum of 5c,
(S_2) UV-vis spectrum of 5c after addition of Cu²⁺ (1 equiv.),
(S_3) UV-vis spectrum of 5c after addition of Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, Ba²⁺ (1 equiv. of each metal ion),
(S_4) UV-vis spectrum of 5c after addition of Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, Ba²⁺ (1 equiv. of each metal ion) and Cu²⁺ (1 equiv.)
(S_5) UV-vis spectrum of 5c after addition of Fe²⁺, Mn²⁺, Co²⁺, Ni²⁺, Zn²⁺ (1 equiv. of each metal ion),
(S_6) UV-vis spectrum of 5c after addition of Fe²⁺, Mn²⁺, Co²⁺, Ni²⁺, Zn²⁺ (1 equiv. of each metal ion) and Cu²⁺ (1 equiv.)
(S_7) UV-vis spectrum of 5c after addition of Al³⁺ (1 equiv.),
(S_8) UV-vis spectrum of 5c after addition of Al³⁺ (1 equiv.) and Cu²⁺ (1 equiv.)
(S_9) UV-vis spectrum of 5c after addition of Ag²⁺, Hg²⁺, Cd²⁺, Pb²⁺ (1 equiv. of each metal ion),
(S_10) UV-vis spectrum of 5c after addition of Ag²⁺, Hg²⁺, Cd²⁺, Pb²⁺ (1 equiv. of each metal ion) and Cu²⁺ (1 equiv.).
3.2 Fluorimetric and spectrophotometric titrations of 5c with Cu^{2+} ions

**Figure S18.** Evolution of fluorescence spectrum of 5c (24 μM solution in CH$_3$CN) upon addition of Cu(ClO$_4$)$_2$ (0 - 1.2 equiv.) (λ$_{ex}$ = 385 nm).

**Figure S19.** (a) Changes of emission intensities at 505 nm plotted against [Cu(ClO$_4$)$_2$]/[5c]$_{tot}$. (b) Job’s plot derived from the titration curve$^2$. Stability constants calculated using SPECFIT$^3$

$\lg(\beta_{Cu(5c)_{2}}) = 14.5 \pm 0.3$, $\lg(\beta_{Cu(5c)}) = 8.0 \pm 0.2$
Figure S20. (a) Evolution of UV–vis spectrum of 5c (60 µM solution in CH$_3$CN) upon addition of Cu(ClO$_4$)$_2$ (0 - 2.3 equiv.). (b) UV-vis spectra of 5c (red), [Cu(5c)$_2$]$^{2+}$ (green) and [Cu(5c)]$^{2+}$ (magenta) calculated using SPECFIT$^1$. (c) Species distribution diagram for the Cu$^{2+}$/5c system in CH$_3$CN calculated using SPECFIT$^1$.

Figure S21. (a) Changes of absorbance at 311 nm plotted against $[\text{Cu(ClO}_4\text{)}_2]/[5\text{c}]_{\text{tot}}$. (b) Job’s plot derived from the titration curve$^2$. 

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Figure S22. (a) Changes of absorbance at 385 nm plotted against [Cu(ClO$_4$)$_2$]/[5c]$_{tot}$. (b) Job’s plot derived from the titration curve$^2$.

Stability constants calculated using SPECFIT$^1$

$\lg(\beta_{\text{Cu} (5c)2}) = 14.5\pm0.2$ , $\lg(\beta_{\text{Cu} (5c)}) = 8.4\pm0.2$
4. Studies of binding metal ions by 10

4.1. Fluorimetric and UV-vis studies of binding metal ions by 10

**Figure S23.** Fluorescence spectra of 10 ([10] = 20 μM) in CH₃CN before and after addition of 4 equiv. of metal perchlorates in CH₃CN (λₑₓ = 390 nm).

**Figure S24.** UV-vis spectra of 10 ([10] = 20 μM) in CH₃CN before and after addition of 4 equiv. of metal perchlorates in CH₃CN.
4.2 Fluorimetric and spectrophotometric titrations of 10 with Cu$^{2+}$ ions

Figure S25. (a) Evolution of fluorescence spectrum of 10 (9 µM solution in CH$_3$CN) upon addition of Cu(ClO$_4$)$_2$ (0 - 0.5 equiv.) ($\lambda_{ex} = 390$ nm). (b) Evolution of luminescence spectrum of 10 (9 µM solution in CH$_3$CN) upon addition of Cu(ClO$_4$)$_2$ (0.5 - 5.7 equiv.) ($\lambda_{ex} = 390$ nm).

Figure S26. Changes of emission intensities at 478 nm plotted against [Cu(ClO$_4$)$_2$]/[10]$_{tot}$. Stability constants calculated using SPECFIT$^1$

$\lg(\beta_{\text{Cu}_2(10)_2}) = 11.3\pm0.2$, $\lg(\beta_{\text{Cu}(10)}) = 6.1\pm0.1$
Figure S27. Evolution of UV–vis spectrum of 10 (54 μM solution in CH$_2$CN) upon addition of Cu(ClO$_4$)$_2$ (0 - 0.5 equiv.). (b) Evolution of UV–vis spectrum of 10 (54 μM solution in CH$_2$CN) upon addition of Cu(ClO$_4$)$_2$ (0.5 - 2.2 equiv.). (c) UV-vis spectra of 10 (red), [Cu(10)$_2$]$^{2+}$ (green) and [Cu(10)]$^{2+}$ (magenta) calculated using SPECFIT$^1$. (d) Species distribution diagram for the Cu$^{2+}$/10 system in CH$_2$CN calculated using SPECFIT$^1$. 
Figure S28. (a) Changes of absorbance at 390 nm plotted against [Cu(ClO₄)₂]/[10]ₜot. (b) Job’s plot derived from the titration curve².

Stability constants calculated using SPECFIT¹

lg(β_{Cu(10)₂}) = 11.7±0.2, lg(β_{Cu(10)}) = 6.4±0.1
4.3 Fluorimetric and spectrophotometric titrations of 10 with Zn$^{2+}$ ions

**Figure S29.** Evolution of fluorescence spectrum of 10 (9 µM solution in CH$_3$CN) upon addition of Zn(ClO$_4$)$_2$ (0 - 1.5 equiv.) ($\lambda_{ex} = 390$ nm).

**Figure S30.** (a) Changes of emission intensities at 478 nm plotted against [Zn(ClO$_4$)$_2$]/[10]$_{tot}$. (b) Job’s plot derived from the titration curve.

Stability constants calculated using SPECFIT$^1$

$\lg(\beta_{Zn(10)4}) = [19.9]$ , $\lg(\beta_{Zn(10)2}) = 10.7 \pm 0.4$
Figure S31. (a) Evolution of UV–vis spectrum of 10 (54 μM solution in CH₃CN) upon addition of Zn(ClO₄)₂ (0 - 0.6 equiv.). (b) UV-vis spectra of 10 (red), [Zn(10)₄]²⁺ (green) and [Zn(10)₂]²⁺ (magenta) calculated using SPECFIT¹. (c) Species distribution diagram for the Zn²⁺/10 system in CH₃CN calculated using SPECFIT¹.

Figure S32. (a) Changes of absorbance at 390 nm plotted against [Zn(ClO₄)₂]/[10]ₐₙₜ. (b) Job’s plot derived from the titration curve². Stability constants calculated using SPECFIT¹

\[ \lg(\beta_{\text{Zn(10)₄}}) = 20.0 \pm 0.4 \], \[ \lg(\beta_{\text{Zn(10)₂}}) = 11.9 \pm 0.2 \]
4.4 NMR titrations of 10 with Zn$^{2+}$ ions

Figure S33. 400 MHz H NMR spectra of 10 in CD$_3$CN at 298 K before (a) and after addition of 0.1 (b), 0.2 (c), 0.3 (d), 0.4 (e), 0.5 (f), 0.6 (g), 0.7 (h) and 0.8 (i) equiv. of zinc perchlorate.
Figure S34. Changes of the chemical shift of NH-proton plotted against $[\text{Zn(ClO}_4)_2]/[10]_{\text{tot}}$.

Figure S35. Changes of the chemical shift of CH$_2$O-proton plotted against $[\text{Zn(ClO}_4)_2]/[10]_{\text{tot}}$.

Figure S36. Changes of the chemical shift of H$_8$(Quin)-proton plotted against $[\text{Zn(ClO}_4)_2]/[10]_{\text{tot}}$. 
5. Supposed mechanism of quenching fluorescence of ligands 10 and 5c

Supposed mechanism of quenching luminescence of ligand 10 by Cu$^{2+}$ ions

Supposed mechanism of quenching luminescence of ligand 5c by Cu$^{2+}$ ions
6. NMR spectra

**Figure S37.** $^1$H NMR spectrum of 4 (CDCl$_3$, 400MHz, 300K).

**Figure S38.** $^{13}$C NMR spectrum of 4 (CDCl$_3$, 400MHz, 300K). (4 quaternary carbon atoms were not unambiguously assigned because of broadening of the signals and low concentration)
Figure S39. $^1$H NMR spectrum of 5a (CDCl$_3$, 400MHz, 300K).

Figure S40. $^{13}$C NMR spectrum of 5a (CDCl$_3$, 400MHz, 300K).
Figure S41. $^1$H NMR spectrum of 5b (CDCl$_3$, 400MHz, 300K).

Figure S42. $^{13}$C NMR spectrum of 5b (CDCl$_3$, 400MHz, 300K).
Figure S43. $^1$H NMR spectrum of 5c (CDCl$_3$, 400MHz, 300K).

Figure S44. $^{13}$C NMR spectrum of 5c (CDCl$_3$, 400MHz, 300K).
Figure S45. $^1$H NMR spectrum of 6 (CDCl$_3$, 400MHz, 300K).

Figure S46. $^{13}$C NMR spectrum of 6 (CDCl$_3$, 400MHz, 300K).
Figure S47. $^1$H NMR spectrum of 7 (CDCl$_3$, 400MHz, 300K).

Figure S48. $^{13}$C NMR spectrum of 7 (CDCl$_3$, 400MHz, 300K).
Figure S49. $^1$H NMR spectrum of 8 (CDCl$_3$, 400MHz, 300K).
Figure S50. $^1$H NMR spectrum of 10 (CDCl$_3$, 400MHz, 300K).

Figure S51. $^{13}$C NMR spectrum of 10 (CDCl$_3$, 400MHz, 300K).
7. References
