molecules

Article

Highly Sensitive and Selective Fluorescent Probes for Cu(II) Detection Based on Calix[4]arene-Oxacyclophane Architectures

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Supplementary Materials

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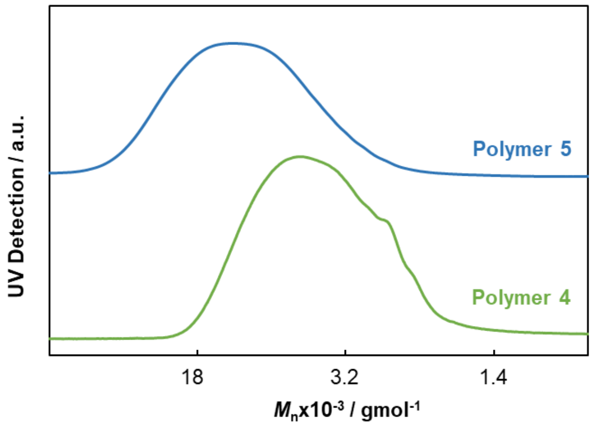


Figure 1. GPC traces of isolated polymers **4** and **5** against monodisperse polystyrene standards (THF as eluent at 35 °C).

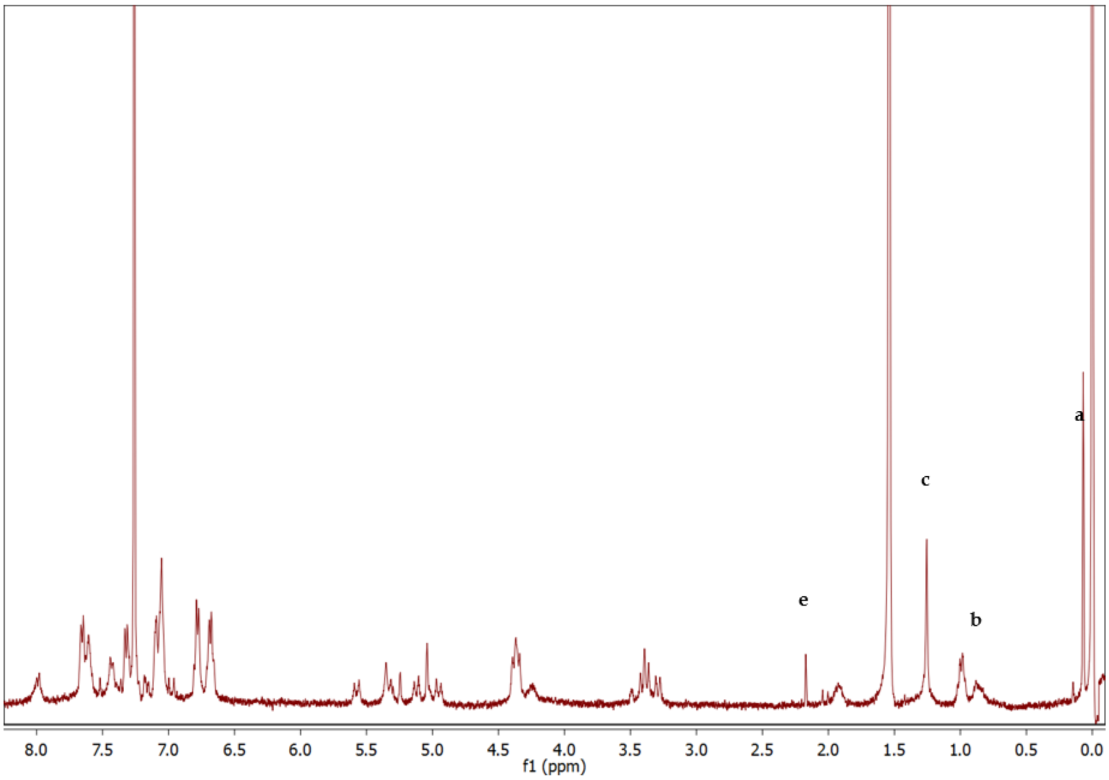


Figure 2. ^{1}H NMR spectrum of polymer **4** in $CDCl_3$ (400 MHz, 25 ºC); [a]silicone grease; [b,c]Apiezon type grease; [d]water; [e]acetone.

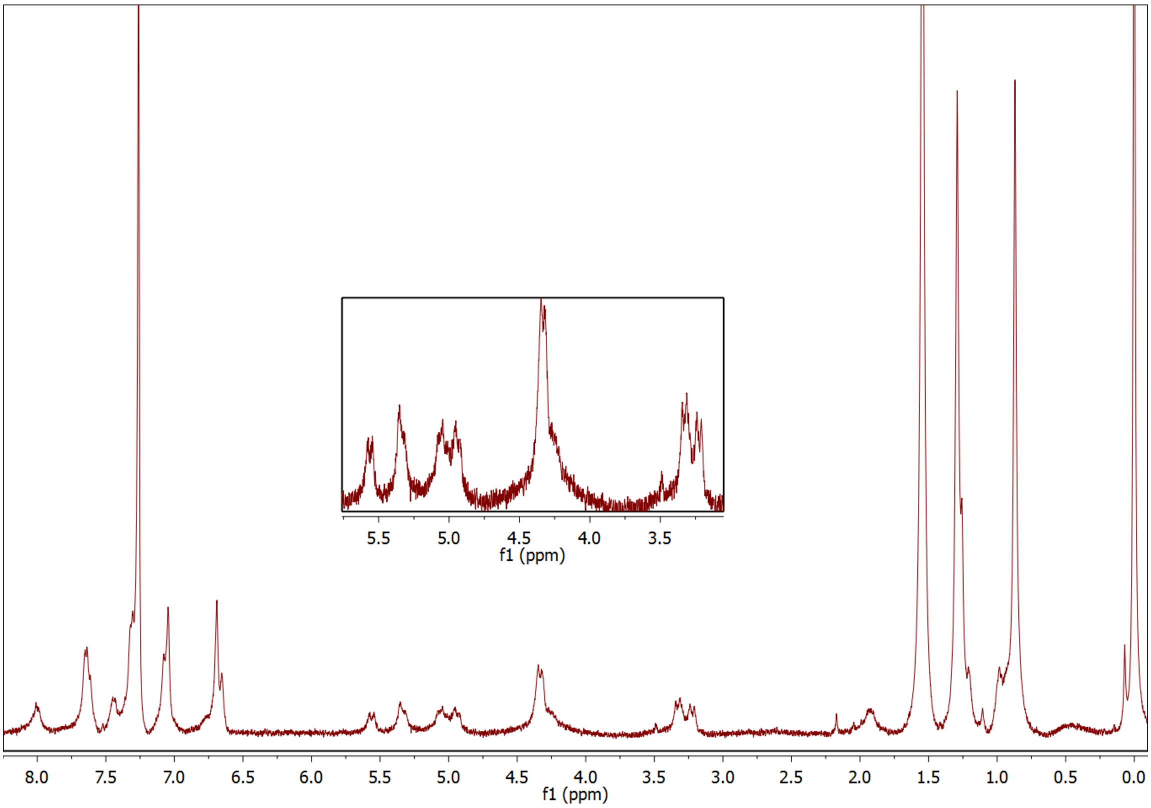


Figure 3. ^1H NMR spectrum of polymer **5** in $CDCl_3$ (400 MHz, 25 °C); [a]silicone grease; [b]Apiezon type grease; [c]water; [d]acetone.

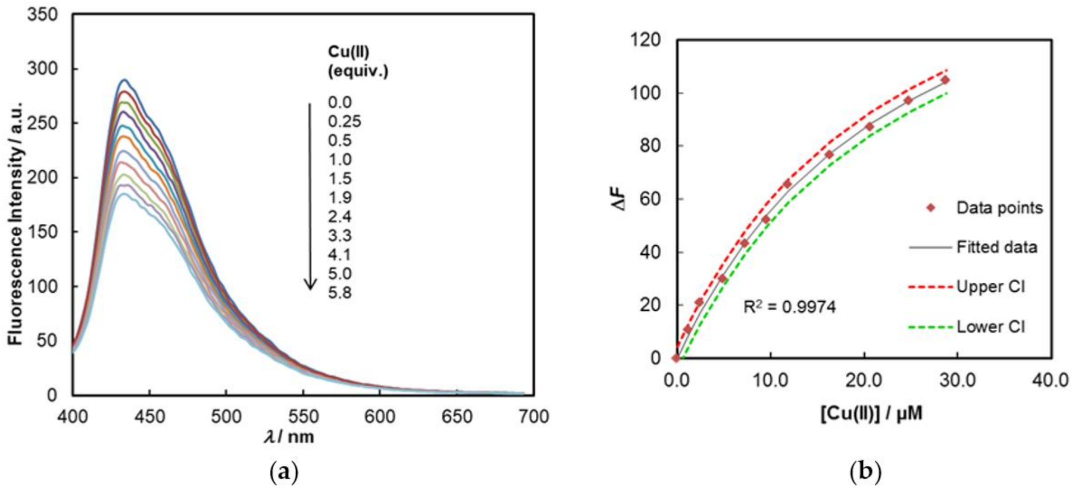
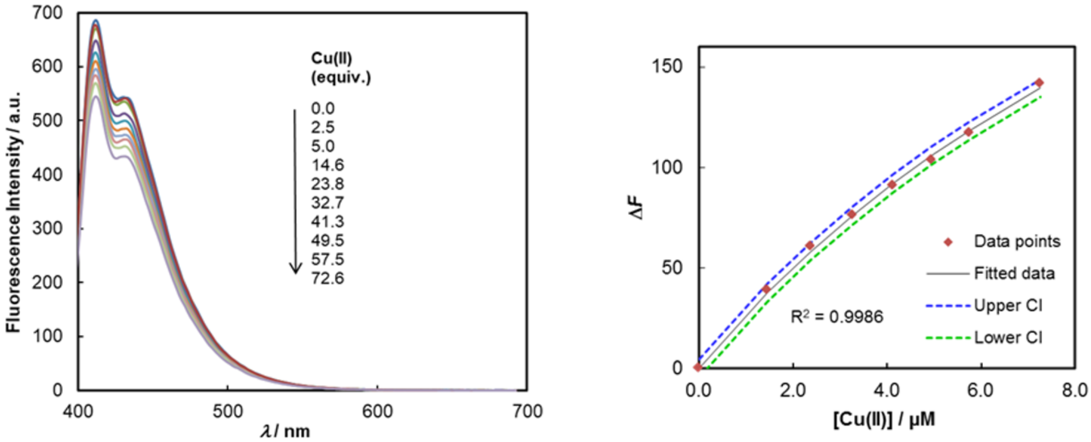


Figure 4. (**a**) Emission spectra of polymer **6** (5.0×10^{-6} M in CH_3CN) upon addition of increasing amounts (0.25 - 5.8 equiv.) of $Cu(ClO_4)_2$ (λ_{exc} = 380 nm); (**b**) Binding isotherm for the fluorimetric titration of **6** with Cu(II) with fitted curve and confidence intervals.



(**a**) (**b**)

Figure 5. (**a**) Emission spectra of **Calix-OCP-2-CBZ** (1.0×10^{-7} M in CH_3CN) upon addition of increasing amounts (2.5 - 72.6 equiv.) of $Cu(ClO_4)_2$ (λ_{exc} = 380 nm); (**b**) Binding isotherm for the fluorimetric titration of **Calix-OCP-2-CBZ** with Cu(II) with fitted curve and confidence intervals.

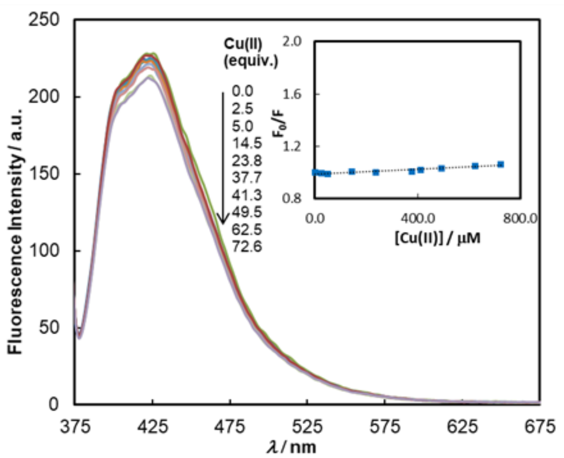


Figure 6. Emission spectra of **bis-Calix-TriPr-2-CBZ** (1.0×10^{-5} M in CH_3CN) upon addition of increasing amounts (2.5 - 72.6 equiv.) of $Cu(ClO_4)_2$ (λ_{exc} = 380 nm). Inset: Plot of F_0/F *vs* [Cu(II)].

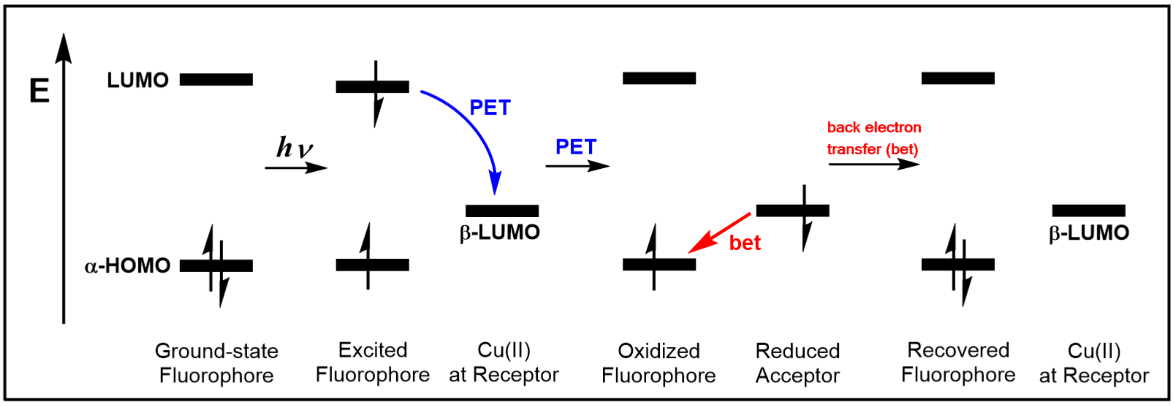


Figure 7. Cartoon illustrating the mechanism of fluorescence quenching by photoinduced electron transfer (PET).

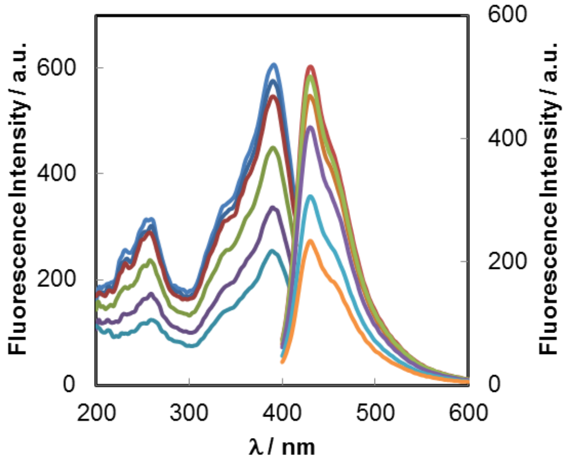


Figure 8. Excitation (left; monitored at 430 nm) and emission (right; λ_{exc} = 380 nm) spectra of polymer **5** (5.0×10^{-6} M in CH_3CN) upon addition of increasing amounts (0.25 - 10 equiv.) of $Cu(ClO_4)_2$.

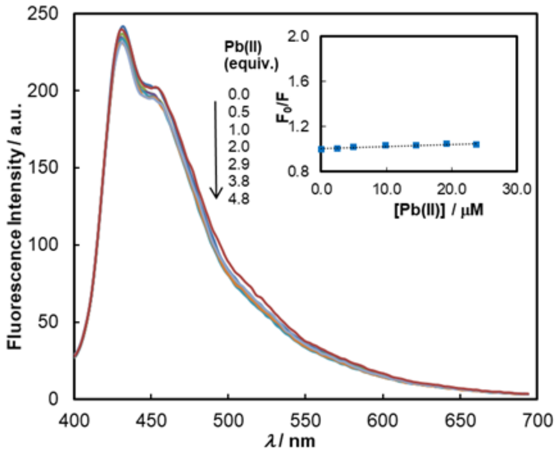


Figure S9. Emission spectra of polymer **5** (5.0×10^{-6} M in CH_3CN) upon addition of increasing amounts (0.5 - 4.8 equiv.) of $Pb(ClO_4)_2$ (λ_{exc} = 380 nm). Inset: Plot of F_0/F *vs* [Pb(II)].

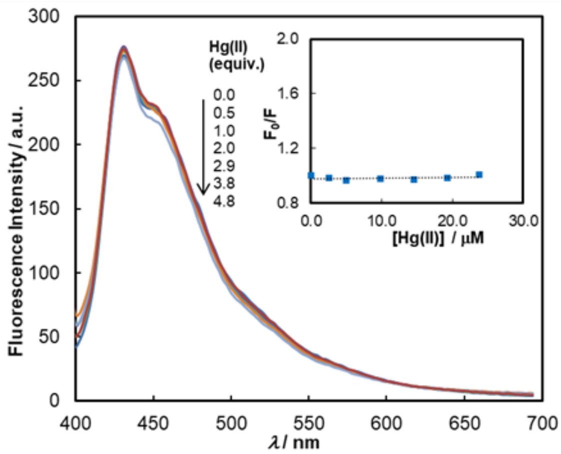


Figure 10. Emission spectra of polymer **5** (5.0×10^{-6} M in CH_3CN) upon addition of increasing amounts (0.5 - 4.8 equiv.) of $Hg(ClO_4)_2$ (λ_{exc} = 380 nm). Inset: Plot of F_0/F *vs* [Hg(II)].

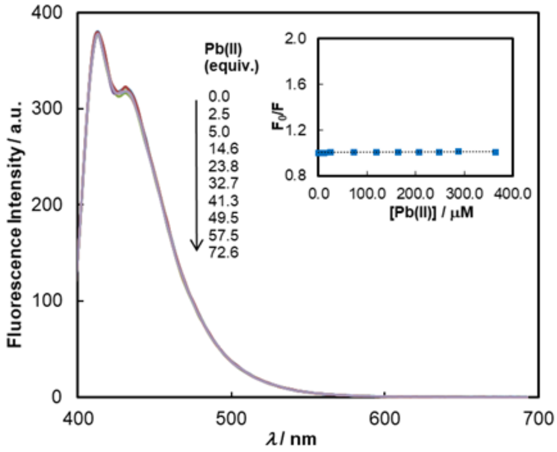


Figure S11. Emission spectra of **Calix-OCP-2-CBZ** (5.0×10^{-6} M in CH_3CN) upon addition of increasing amounts (2.5 - 72.6 equiv.) of $Pb(ClO_4)_2$ (λ_{exc} = 380 nm). Inset: Plot of F_0/F *vs* [Pb(II)].

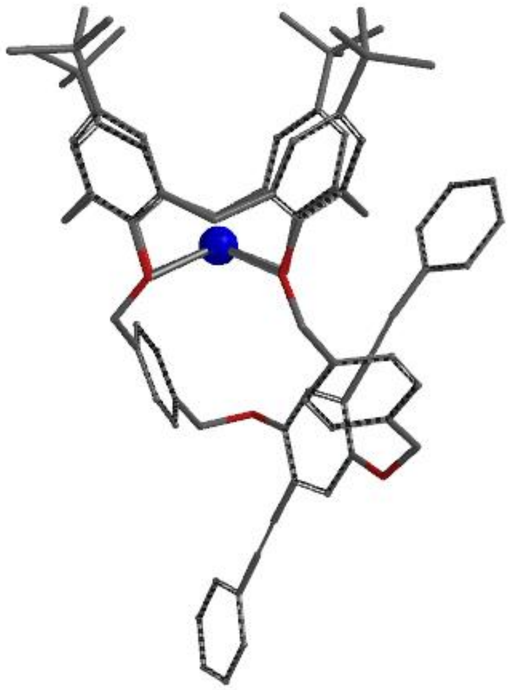


Figure 12. Optimised structure of Calix-OCP-Pb(II) complex (model). DFT calculations run at the B3LYP/6-31G(d) level of theory in vacuum, using the LANL2DZ pseudopotential for Pb [1]. Hydrogens omitted for clarity. Colour codes for elements: red = oxygen, grey = carbon, blue = lead.

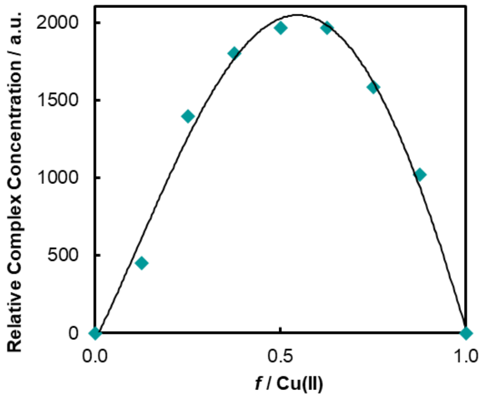


Figure 13. Job plot for complex formation between polymer **4** and Cu(II) in CH_3CN (at constant 1.0 x 10^{-5} M total concentration) as obtained from changes in fluorescence (λ_{exc} = 380 nm).

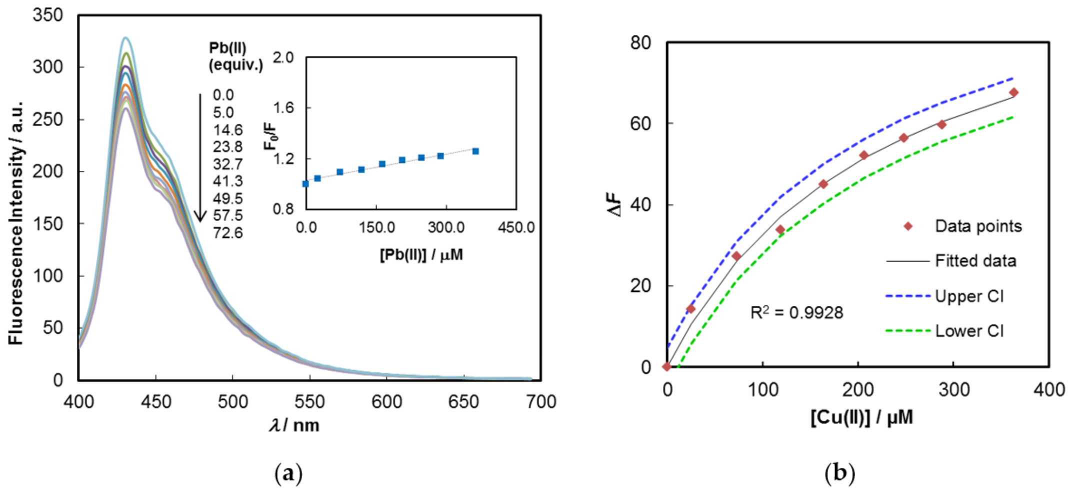


Figure 14. (**a**) Emission spectra of polymer **4** (5.0 x 10^{-6} M in CH_3CN) upon addition of increasing amounts (5.0 - 72.6 equiv.) of $Pb(ClO_4)_2$ (λ_{exc} = 380 nm); (**b**) Binding isotherm for the fluorimetric titration of **4** with Pb(II) with fitted curve and confidence intervals.

Determination of stoichiometry of complexes from Job plots [2]

Table 1. Experimental values of Σc/cMAX of the Job plot for polymer **5**.

nCu(II)/mol	x Cu(II)	F	[Polymer 5]/M	(F_0-F)/F_0 x [Polymer 5]/nM	c/c_{max}
0.00E+00	0.00	375.61	1.00E−05	0.00	0.00
2.50E−09	0.13	319.10	8.75E−06	1316.43	0.53
5.00E−09	0.25	265.05	7.50E−06	2207.71	0.89
7.50E−09	0.38	228.09	6.25E−06	2454.67	0.99
1.00E−08	0.50	188.58	5.00E−06	2489.68	1.00
1.25E−08	0.63	160.00	3.75E−06	2152.60	0.86
1.50E−08	0.75	112.83	2.50E−06	1749.05	0.70
1.75E−08	0.88	69.78	1.25E−06	1017.78	0.41
2.00E±08	1.00	18.17	0.00E+00	0.00	0.00
				Σ(c/c_{max}) =	**5.38**

x - molar fraction; F_0 is the fluorescent intensity of polymer **5** in the absence of copper cation; F is the fluorescent intensity recorded in the presence of metal cation; c is the concentration.

Table 2. Experimental values of Σc/cMAX of the Job plot for polymer **4**.

nCu(II)/mol	x Cu(II)	F	[Polymer 4]/M	(F_0-F)/F_0 x [Polymer 4]/nM	c/c_{max}
0.00E+00	0.00	450.90	1.00E−05	0.00	0.00
2.50E−09	0.13	427.24	8.75E−06	450.09	0.23
5.00E−09	0.25	365.43	7.50E−06	1393.65	0.71
7.50E−09	0.38	318.27	6.25E−06	1802.19	0.92
1.00E−08	0.50	270.05	5.00E−06	1965.93	1.00
1.25E−08	0.63	210.15	3.75E−06	1962.81	1.00
1.50E−08	0.75	159.45	2.50E−06	1584.11	0.81
1.75E−08	0.88	75.25	1.25E−06	1020.88	0.52
2.00E−08	1.00	2.23	0.00E+00	0.00	0.00
				Σ(c/c_{max}) =	**5.18**

x - molar fraction; F_0 is the fluorescent intensity of polymer **4** in the absence of copper cation; F is the fluorescent intensity recorded in the presence of metal cation; c is the concentration.

References

1. Spartan'14 Molecular Modeling Program, Wavefunction, Inc., Irvine, CA, 2014.
2. Olson, E.J.; Bühlmann, P. Getting More out of a Job Plot: Determination of Reactant to Product Stoichiometry in Cases of Displacement Reactions and n:n Complex Formation. *J. Org. Chem.* **2011**, 76, 8406–8412.