A novel molecular luminescent sensor for metal ions using deprotonated tetramethylpropane-1,1,3,3-tetracarboxylate as ionophore

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Luminescent properties of the supramolecular complex, $[Re(bpy)(CO)_3\{py\text{-}CH[CH(COOMe)_2]_2\}]^+$ (**3**, bpy = 2,2′-bipyridine), containing a novel ionophore precursor, $py\text{-}CH[CH(COOMe)_2]_2$ (**1**), with two adjacent dimethyl malonate moieties joined together by a pyridine substituted methylene bridge, are found to respond selectively to Ba^{2+} upon deprotonation of the two malonate moieties.

Design and synthesis of selective and sensitive molecular sensors for biologically, clinically and environmentally important metal ions, anions and neutral species is one of the most challenging fields in supramolecular chemistry.[1] Although the ability of various molecular hosts, such as crown ethers and cryptands,[2] polyamines and amides,[1g,3] xanthones,[4] calix[4]arenes,[5] *etc.*, to act as selective receptors for metal ions as well as anions has been well studied, exploration of new ionophores showing advantageous features over these established systems is still receiving much research attention. One of the common drawbacks of most established ionophores is their elaborated structure, so that they usually require multiple steps to synthesize with relatively low yields. In this work, we report a high-yield one-pot synthesis of a novel ionophore precursor, 2-pyridyltetramethylpropane-1,1,3,3-tetracarboxylate {py-CH[CH(COOMe)_2]_2, **1**} as well as its Pd(II) and Re(I) complexes, $[PdCl_2\{py\text{-}CH[CH(COOMe)_2]_2\}_2]$ (**2**) and $[Re(bpy)(CO)_3\{py\text{-}CH[CH(COOMe)_2]_2\}]^+$ (**3**, bpy = 2,2′-bipyridine). The ionophore precursor **1** contains two dimethyl malonate moieties joined together by a pyridine substituted methylene bridge. Under basic conditions, the two adjacent deprotonated malonates are found to function as ionophores for metal ion binding. The use of carboxylate and malonate groups as ionophores for metal ions in chemical sensing have already been explored by numerous researchers. For example, Tsien *et al.*[6] have reported a number of selective Ca^{2+} supramolecular sensors using multiple carboxylic groups for metal chelation. Mutou *et al.*[7] have recently used 2,6-disubstituted pyridines with bis(alkoxyethyl)malonate subunits as hosts for alkali metals, but poor guest selectivity was noted. In this study, the Re(I) organometallic complex (**3**) is found to display a luminescent response to metal ion (especially Ba^{2+}) binding in the presence of a base. The simple and high-yield synthesis of **1**, together with its convenient incorporation into coordination and organometallic systems, makes it an attractive receptor moiety for supramolecular metal ion sensing applications.

Experimental

Dimethyl malonate, diethylamine, pyridine-4-carboxaldehyde and Re(CO)_5Br were obtained from Aldrich. All solvents used were of analytical grade. Acetonitrile used in spectrofluorometric titration was purified by stirring with $KMnO_4$, followed by distillation under nitrogen. UV-Vis spectra were measured on a Hewlett Packard 8452A ultraviolet visible diode array spectrophotometer. ^1H NMR spectra were recorded using a Varian YH300 300 MHz NMR spectrometer. Emission spectra were recorded using a Horiba FluoroMax-3 spectrofluorometer with 2 nm slit width and 0.5 s integration time.

Syntheses

2-Pyridyltetramethylpropane-1,1,3,3-tetracarboxylate {py-CH[CH(COOMe)_2]_2, 1}. A solution of dimethyl malonate (5.00 g, 37.8 mmol), diethylamine (0.28 g, 3.8 mmol) and pyridine-4-carboxaldehyde (2.03 g, 19.0 mmol) in absolute ethanol (50 ml) was stirred for 16 h followed by reflux for a further 6 h. A red solution was obtained. Ethanol was distilled off under reduced pressure and diethyl ether (300 ml) was added to the resulting deep red oil. The mixture was kept at 0 °C overnight to yield **1** as a pink precipitate, which was collected by filtration and washed by cold diethyl ether (2 × 20 ml). The product was pure enough for use in further reactions. Yield: 80%. ^1H NMR (300 MHz, CDCl_3): δ 8.50 (2H, d, pyridine-H), 7.20 (2H, d, pyridine-H), 4.25–4.10 (3H, m, isopropyl-CH), 3.70 (6H, s, methyl malonate-CH_3), 3.50 (6H, s, methyl malonate-CH_3). ES-MS (+ve mode): m/z 354 $[M + H]^+$.

[PdCl_2{py-CH[CH(COOMe)_2]_2}_2] (2). A mixture of [Pd(MeCN)_2Cl_2] (0.10 g, 0.39 mmol) and **1** (0.27 g, 0.78 mmol) in acetonitrile (20 ml) was refluxed for 3 h. The resultant mixture was evaporated to dryness under reduced pressure and the yellow residue was washed with diethyl ether (20 ml) and redissolved in CH_2Cl_2 (10 ml). Slow diffusion of diethyl ether into the CH_2Cl_2 solution yielded **2** as pale yellow needle-shaped crystals suitable for X-ray crystallographic study. Yield: 46%. ^1H NMR (300 MHz, CDCl_3): δ 8.70 (2H, d, pyridine-H), 7.30 (2H, d, pyridine-H), 4.25–4.10 (3H, m, isopropyl-CH), 3.70 (6H, s, methyl malonate-CH_3), 3.55 (6H, s, methyl malonate-CH_3).

[Re(bpy)(CO)_3{py-CH[CH(COOMe)_2]_2}](PF_6) (3). A mixture of [Re(bpy)(CO)_3Br] (0.10 g, 0.2 mmol) and $AgCF_3SO_3$

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(0.05 g, 0.2 mmol) was refluxed in THF (30 ml) under nitrogen for 3 h, which was then filtered under nitrogen into a THF (20 ml) solution of **1** (0.07 g, 0.2 mmol). The resultant solution was refluxed under nitrogen for 24 h to yield a red solution. [^{n}Bu$_4$N][PF$_6$] (0.10 g, 0.26 mmol) was then added and the mixture was refluxed for a further 1 h. The resultant solution was evaporated under reduced pressure to 5 ml and diethyl ether (100 ml) was added to precipitate **3** as a yellow solid. The product was collected by filtration, air-dried and recrystallized from acetonitrile–diethyl ether as bright yellow needles. Yield: 80% ^{1}H NMR (300 MHz, CDCl$_3$): δ 9.10 (2H, d, bpy-H), 8.85 (2H, d, bpy-H), 8.35 (2H, t, bpy-H), 8.05 (2H, d, pyridine-H), 7.80 (2H, t, bpy-H), 4.15–4.00 (3H, m, isopyropyl-CH), 3.70 (6H, s, methyl malonate-CH$_3$), 3.50 (6H, s, methyl malonate-CH$_3$). ES-MS (+ve mode): m/z 780 [M]$^+$, 427 [M]– py-CH{CH(COOMe)$_2$}$_2$]$^+$.

X-Ray crystallography

Geometric and intensity data for **2** were collected on a Bruker Axs SMART 1000 CCD area detector using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The collected frames were processed with the software SAINT[8] and an absorption correction was applied (SADABS[9]) to the collected reflections. The structure was solved by direct methods (SHELXTL[10]) in conjunction with standard difference Fourier techniques and subsequently refined by full-matrix least-square analyses on F^2. All non-hydrogen atoms were assigned with anisotropic displacement parameters. The hydrogen atoms were generated in their idealized positions and allowed to ride on the respective carbon atoms. Crystal data and other experimental details are given in Table 1.

CCDC reference number 177849. See http://www.rsc.org/suppdata/nj/b1/b108087n/ for crystallographic data in CIF or other electronic format.

Spectrofluorometric titration

All spectrofluorometric titrations were carried out in acetonitrile containing 0.03 M [^{n}Bu$_4$N][PF$_6$] as supporting electrolyte. All metal salts used were perchlorate salts. The binding constant, K_S, for the interaction between the *in situ* deprotonated [Re(bpy)(CO)$_3${py-CH[C(COOMe)$_2$]$_2$}]$^-$ and metal ion in

Table 1 Crystallographic data for [PdCl$_2${py-CH[CH(COOMe)$_2$]$_2$}$_2$] (**2**)

Formula	C$_{32}$H$_{38}$Cl$_2$N$_2$O$_{16}$Pd
M	883.94
Crystal system	Monoclinic
Space group	P2$_1$/n
a/Å	9.5535(6)
b/Å	9.6338(7)
c/Å	21.176(1)
β/°	100.831(1)
U/Å^3	1914.3(2)
Z	2
T/K	293
μ (Mo-Kα)/mm^{-1}	0.697
Reflections collected	10918
Unique reflections	4314
R$_{int}$	0.023
Observed reflections [$I > 2\sigma(I)$]	4314
R$_1$	0.0393
wR$_2$	0.1182

acetonitrile was estimated from eqn. (1), which assumes a 1 : 1 ionophore-metal ion interaction:

$$\frac{I_F^o}{(I_F - I_F^o)} = \left[\frac{a}{(b-a)}\right]\left[\frac{1}{K_S[M]+1}\right] \quad (1)$$

where I_F^o and I_F are the luminescence intensity of [Re(bpy)(CO)$_3${py-CH[C(COOMe)$_2$]$_2$}]$^-$ with and without metal ion, respectively, M is the concentration of metal ion in acetonitrile, a and b are constants. The binding constant K_S was estimated from the ratio between the y intercept and the slope of the straight line obtained by plotting $I_F^o/(I_F - I_F^o)$ *vs.* [M]$^{-1}$.
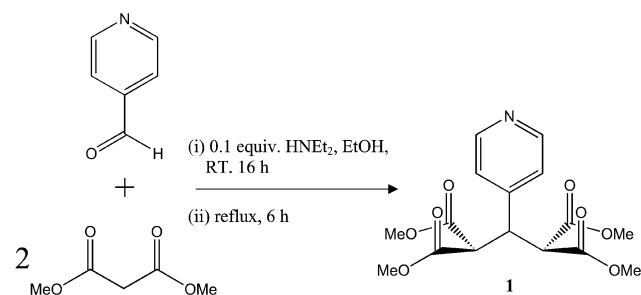
Scheme 1 One-pot synthesis of 2-pyridyltetramethylpropane-1,1,3,3-tetracarboxylate {py-CH[CH(COOMe)$_2$]$_2$} (**1**).
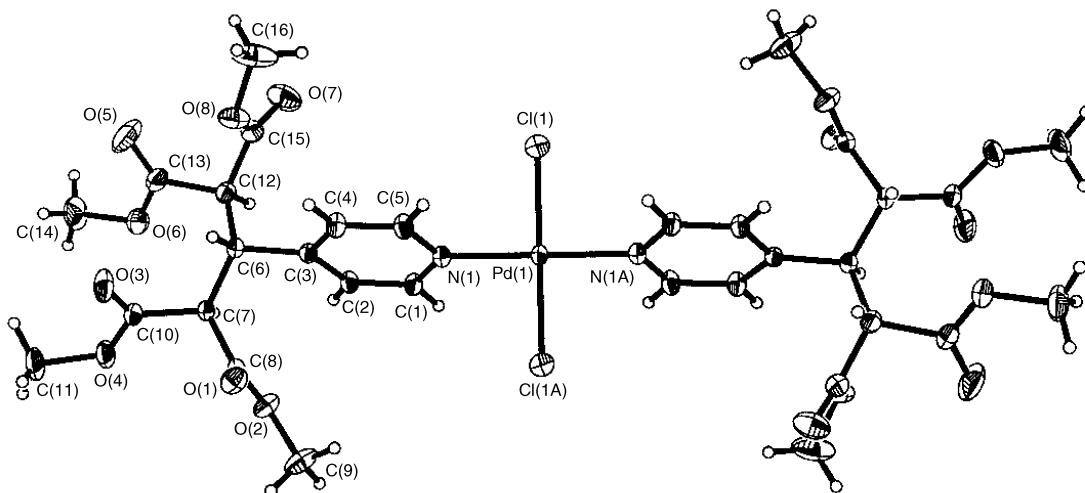

Fig. 1 Perspective view of [PdCl$_2${py-CH[CH(COOMe)$_2$]$_2$}$_2$] (**2**). Selected bond lengths (Å) and angles (°): N(1)–Pd(1) 2.019(3), Cl(1)–Pd(1) 2.274(1), C(3)–C(6) 1.520(4), C(6)–C(7) 1.562(4), C(6)–C(12) 1.553(4); N(1)–Pd(1)–Cl(1) 89.86(8), C(12)–C(6)–C(7) 111.9(2), O(1)–C(8)–C(7) 124.1(3), O(3)–C(10)–C(7) 124.9(3), O(5)–C(13)–C(12) 124.2(4), O(7)–C(15)–C(12) 125.2(4).

Results and discussion

2-Pyridyltetramethylpropane-1,1,3,3-tetracarboxylate (**1**) was conveniently synthesized from pyridine-4-carboxaldehyde and dimethyl malonate in ethanol (Scheme 1) on the gram scale and was characterized by ^{1}H NMR and electrospray MS. The Pd(II) complex **2**, was synthesized from **1** and Pd(MeCN)$_2$Cl$_2$ in acetonitrile. The structure of **2** was ascertained by X-ray crystallography (Fig. 1). The Pd(II) centre adopted a square-planar geometry with two chloro and two py-CH[CH(COOMe)$_2$]$_2$ units arranged in a *trans* configuration. The two py-CH[CH(COOMe)$_2$]$_2$ ligands are coordinated to Pd(II) *via* their pyridine N atom. Lengths of the Pd(II)–N bonds were within the normal range of typical Pd(II)-pyridine complexes.

The Re(I) complex, **3** was synthesized from [Re(bpy)(CO)$_3$(CF$_3$SO$_3$)] and **1** in refluxing THF. Recrystallization from acetonitrile–diethyl ether gave complex **3** as a bright yellow crystalline solid. Complex **3** displays a characteristic MLCT absorption at 360 nm ($\varepsilon = 1371$ M^{-1} cm^{-1}) in acetonitrile, which upon photoexcitation, produces the typical ^{3}MLCT emission of Re(I) tricarbonyl polypyridine systems[11] at 556 nm. The ^{3}MLCT emission of **3** was quenched and slightly red-shifted to 560 nm by the addition of 2 equiv. of [^{n}Bu$_4$N]OH (Fig. 2). Such a change in luminescent properties is attributable to the deprotonation of the two malonate protons on the py-CH[CH(COOMe)$_2$]$_2$ ligand. Negative charges on the resultant py-CH[C(COOMe)$_2$]$_2{}^{2-}$ moieties quench the Re(I)-bpy ^{3}MLCT luminescence *via* a photo-induced electron transfer (PET) mechanism[1d,2h,3a,12] (Scheme 2). Deprotonation of the two malonate protons was confirmed by electrospray MS. Fig. 3 shows the electrospray mass spectrum of the deprotonated [Re(bpy)(CO)$_3$\{py-CH[C(COOMe)$_2$]$_2$\}]$^-$ species, produced *in situ* from **3** and [^{n}Bu$_4$N]OH, showing a parent ion at m/z 778 in anionic mode.
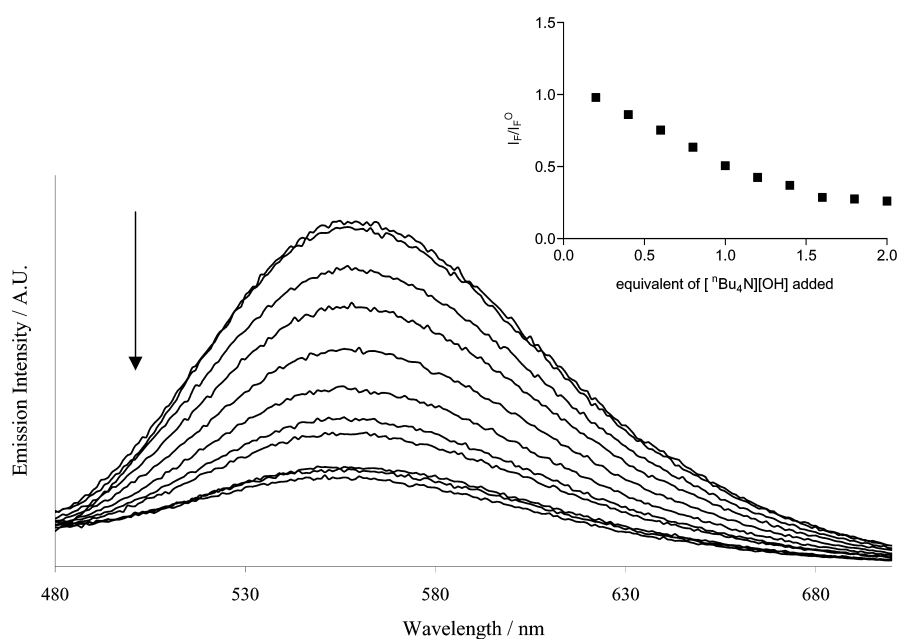
Fig. 2 Spectrofluorometric titration of [Re(bpy)(CO)$_3$\{py-CH[CH(COOMe)$_2$]$_2$\}]$^+$ (**3**) by [^{n}Bu$_4$N]OH in acetonitrile. Change in luminescence intensity at 556 nm with respect to amount of [^{n}Bu$_4$N]OH added is shown in the inset. Quenching of the ^{3}MLCT emission leveled off after addition of 2 equiv. of base.
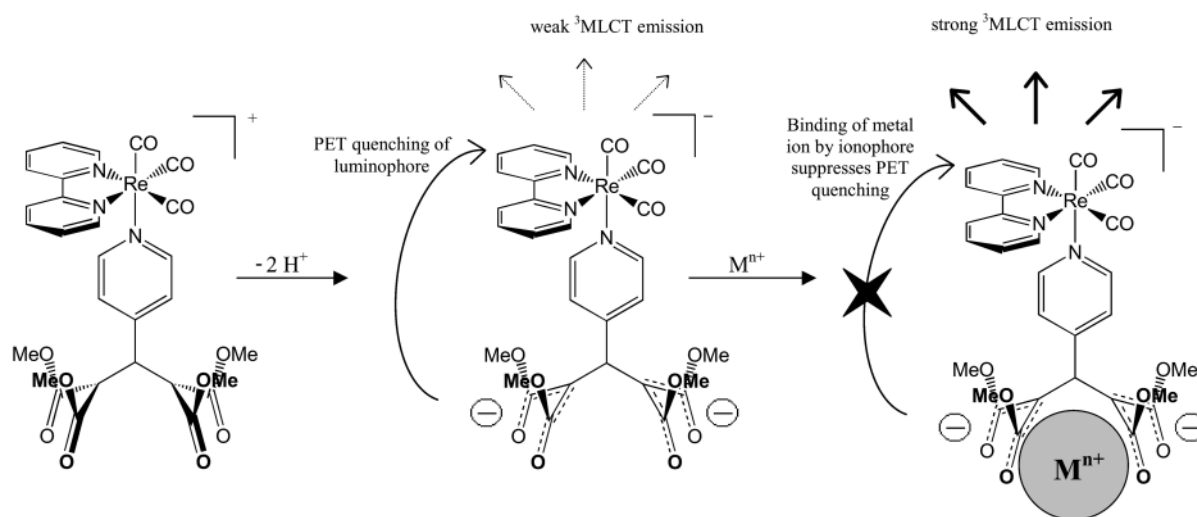
Scheme 2 Generation of ionophore by deprotonation of the py-CH[CH(COOMe)$_2$]$_2$ moiety and PET sensing mechanism of [Re(bpy)(CO)$_3$\{py-CH[C(COOMe)$_2$]$_2$\}]$^-$.

Fig. 3 Electrospay mass spectrum (anionic mode) of $[Re(bpy)(CO)_3\{py\text{-}CH[CH(COOMe)_2]_2\}]^+$ (**3**) in acetonitrile after addition of 2 equiv. of $[^nBu_4N]OH$, showing $[M]^- = [Re(bpy)(CO)_3\{py\text{-}CH[C(COOMe)_2]_2\}]^-$ at m/z 778.1. Simulation of the $[M]^-$ is shown in the inset.

The ^{3}MLCT luminescence of $[Re(bpy)(CO)_3\{py\text{-}CH[C(COOMe)_2]_2\}]^-$ was restored by the addition of metal ions. Fig. 4 shows a typical spectrofluorometric titration of *in situ* generated $[Re(bpy)(CO)_3\{py\text{-}CH[C(COOMe)_2]_2\}]^-$ by Ba^{2+} in 0.03 M $[^nBu_4N][PF_6]$ in acetonitrile. Alkali metals (Li^+, Na^+, K^+ and Cs^+), alkaline earth metals (Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}) and transition metals (Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+}) were found to restore the ^{3}MLCT emission of complex **3** at 556 nm. Addition of metal ions to un-deprotonated complex **3** did not produce any observable change in absorption and emission spectra. Such luminescent response of deprotonated complex **3** is most probably caused by the binding of metal ions by the two deprotonated malonate moieties of $[Re(bpy)(CO)_3\{py\text{-}CH[C(COOMe)_2]_2\}]^-$, which ties up their negative charges and suppresses the PET quenching of the Re(I)-bpy luminophore (Scheme 2).

Fig. 5 shows the $I_F^o/(I_F - I_F^o)$ *vs.* $1/[M]$ plots for all the tested metals. The estimated binding constants for the interaction between $[Re(bpy)(CO)_3\{py\text{-}CH[C(COOMe)_2]_2\}]^-$ and the various metal ions are tabulated in Table 2. For alkali and alkaline earth metals, the generally good linear fit of the $I_F^o/(I_F - I_F^o)$ *vs.* $1/[M]$ plots suggests a 1 : 1 interaction between the metal ions and the ionophore. Although the general order of metal ion affinity follows: alkaline earth metals > alkali metals, indicating the relative importance of charge density of the metal ion in the ionophore-metal ion interaction, the order of K_S within each group does not corresponds well with the order of ionic radius of the metal ions. The order of K_S in the alkali metals is $Na^+ > Li^+ > K^+ > Cs^+$, while that in the alkaline earth metals is $Ba^{2+} > Mg^{2+} > Sr^{2+} > Ca^{2+}$. This behaviour is in contrast to neutral ionophores having a well-defined binding cavity such as crown ethers and cryptands,
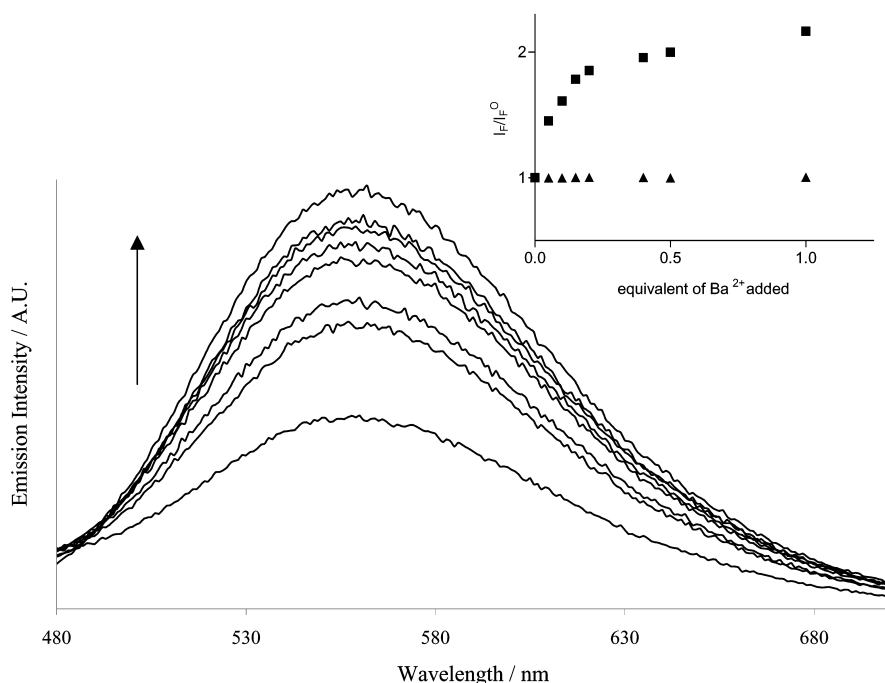

Fig. 4 Spectrofluorometric titration of *in situ* generated $[Re(bpy)(CO)_3\{py\text{-}CH[C(COOMe)_2]_2\}]^-$ (3.33×10^{-5} M) by $Ba(ClO_4)_2$ in 0.03 M $[^nBu_4N][PF_6]$ in acetonitrile. The inset shows the change in luminescent intensity of the deprotonated $[Re(bipy)(CO)_3\{py\text{-}CH[C(COOMe)_2]_2\}]^-$ (■) and the un-deprotonated $[Re(bipy)(CO)_3\{py\text{-}CH[CH(COOMe)_2]_2\}]^+$ (▲) at 560 nm with respect to the amount of Ba^{2+} added.
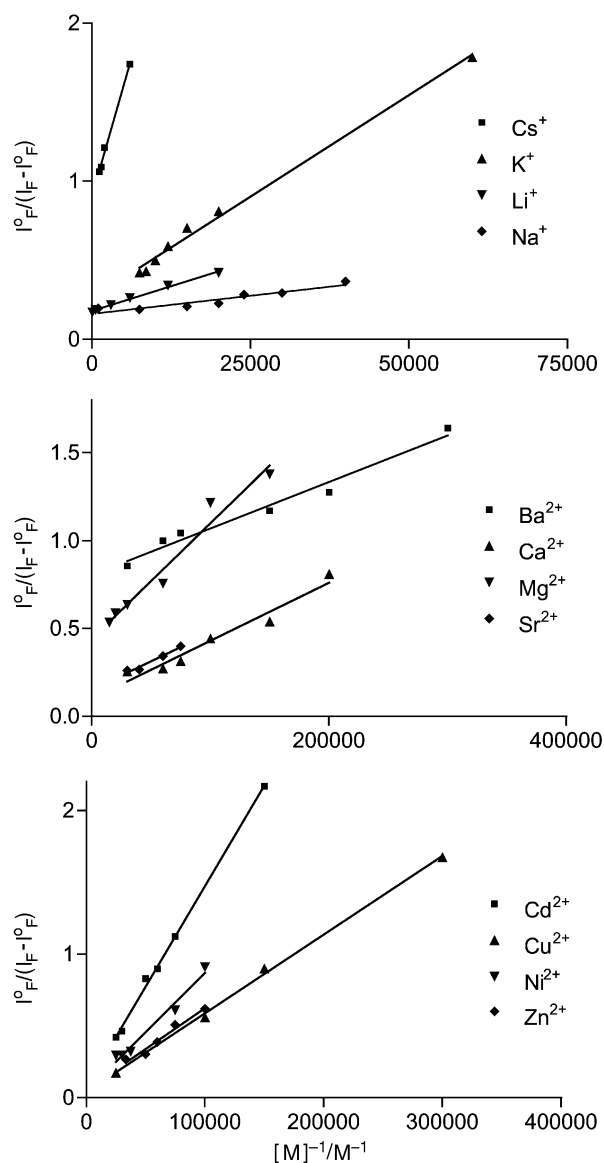
Fig. 5 $I_F^o/(I_F - I_F^o)$ vs. $1/[M]$ plots for all metals that were able to restore ^{3}MLCT emission of *in situ* deprotonated complex **3** in acetonitrile (with 0.03 M [^{n}Bu$_4$N][PF$_6$] as supporting electrolyte). Concentration of [Re(bpy)(CO)$_3${py-CH[C(COOMe)$_2$]$_2$}]$^-$ was 3.33×10^{-5} M in all spectrofluorometric titrations.

Table 2 Binding constants K_S for the interaction between [Re(bpy)-(CO)$_3${py-CH[C(COOMe)$_2$]$_2$}]$^-$ and various metal ions in 0.03 M [^{n}Bu$_4$N][PF$_6$] in acetonitrile

Metal ion	K_S/M^{-1a}
Ba^{2+}	$3.61 \pm 0.85 \times 10^5$
Mg^{2+}	$6.67 \pm 0.35 \times 10^4$
Sr^{2+}	$4.64 \pm 0.51 \times 10^4$
Na$^+$	$3.88 \pm 0.19 \times 10^4$
Ca^{2+}	$3.02 \pm 0.99 \times 10^4$
Zn^{2+}	$2.44 \pm 0.98 \times 10^4$
Li$^+$	$1.41 \pm 0.06 \times 10^4$
K$^+$	$9.96 \pm 1.49 \times 10^3$
Cu^{2+}	$8.00 \pm 4.36 \times 10^3$
Cs$^+$	$6.43 \pm 0.67 \times 10^3$
Cd^{2+}	$4.74 \pm 1.77 \times 10^3$
Ni^{2+}	$3.98 \pm 4.09 \times 10^3$

^{a} Standard derivation in K_S was estimated from the standard derivations ($P < 0.05$) in slope and y intercept of the $I_F^o/(I_F - I_F^o)$ vs. $1/[M]$ plots for the metal fitted by eqn. (1), assuming a 1 : 1 ionophore-metal ion interaction.

where binding strength between metal ions and the ionophores displays clear correlation with the size of the metal ions.[2a–d] The cause of the present complicated trends in K_S is not fully understood but should be attributable, at least to a certain extent, to the open framework and anionic nature of the binding cavity of the fluoroionophore. Binding of metal ions is not achieved by any particular donor atom, but by the two adjacent deprotonated malonate groups with delocalized negative charges. Factors other than size and charge density of the metal ion may also play significant roles in determining metal ion-binding cavity interactions.

Comparing to the alkali and alkaline earth metals, the new fluoroionophore shows remarkably low affinities for transition metals. This is in contrast with the generally good chelating properties of 1,3-dicarbonyl and β-ketoester functionalities towards transition metals, and is probably caused by the special conformation of the two malonate moieties in the ionophore, which does not allow them to coordinate with transition metals in the usual juxtaposed configuration. The relatively poorer fits of the binding data, especially at excesses of metal ion or fluoroionophore, to the 1 : 1 ionophore-metal ion interaction model also suggests possible binding of multiple metal ions by the open binding cavity of the fluoro-ionophore or even complex interactions involving multiple metal ions and fluoroionophore anions. Nevertheless, from the metal binding study, the new ionophore is found to possess a special affinity for Ba^{2+}, as its binding constant K_S ($3.61 \pm 0.85 \times 10^5$ M^{-1}) is 5.4- to 155-fold greater than for the rest of the metal ions tested. The apparent lack of guest selectivity of a conceptually related host reported by Mutou *et al.*,[7] which involved two 2,6-bis(2,2′-dicarbalkoxy-ethyl)pyridines coordinating *trans* to Pd(II), is probably due to the wide separation between the two alkyl malonate moieties and the fact that un-deprotonated malonates were used. The binding cavity formed might be too big for effective metal ion interaction and there was no coulombic interaction between the ionophore and metal ion to assist metal binding.

Our present work demonstrated the ability of a new iono-phore, py-CH[C(COOMe)$_2$]$_2^{2-}$, to use its two adjacent, spe-cially arranged, deprotonated malonates to generate a host cavity for selective metal binding. The binding mechanism itself can be very conveniently coupled to any PET luminescent sensing device for transduction of the binding interaction into an easily measurable luminescence signal. Work is in progress to better understand the mode of interaction between metal ions and the dimalonate binding cavity and to modify the dimension and donor atoms in the binding cavity in order to finetune the metal ion selectivity of the ionophore.

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