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A coumarin–thiourea conjugate as a fluorescent probe for Hg(II) in aqueous media with a broad pH range 2–12†

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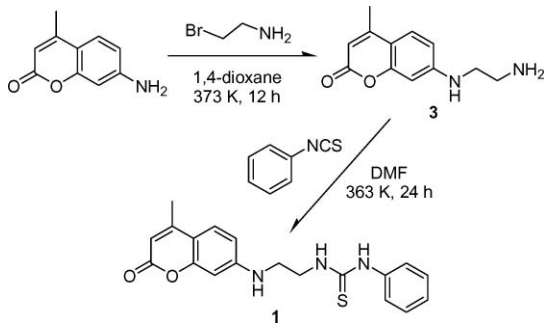
A coumarin–thiourea conjugate (**1**) behaves as a highly selective fluorescent probe for Hg^{2+} in aqueous media. The probe **1** shows selective and quantitative fluorescence decrease upon Hg^{2+} addition in aqueous media with a broad pH range, 2–12. *Ab initio* molecular orbital calculations reveal that the fluorescence decrease of **1** upon Hg^{2+} addition is promoted by a Hg^{2+}-induced desulfurization of the thiourea moiety, leading to a decrease in an intramolecular charge transfer (ICT) character of the excited-state coumarin moiety.

Introduction

Hg^{2+} is one of the most hazardous components in the environment.[1] The design and development of fluorescent Hg^{2+} probes has therefore attracted a great deal of attention.[2] A vast variety of Hg^{2+} probes have been proposed so far;[3] however, most of the probes act only in organic media. Hg^{2+} probes capable of acting in aqueous media have also been proposed; however, many of these probes show insufficient selectivity for Hg^{2+}.[4] Design of Hg^{2+} probes with high selectivity in aqueous media is therefore of current focus. In addition, Hg^{2+} exists in various places such as living organisms, soil, rivers, and seas.[5] Versatile Hg^{2+} probes must therefore be applicable to the samples with high salt concentration and a broad pH range. Several Hg^{2+} probes showing high selectively in aqueous media even with high salt concentration have been proposed; however, most of these probes act only at a neutral pH,[6] and only a few probes act at an acidic–neutral pH.[7]

The Hg^{2+}-induced desulfurization of a thiocarbonyl group is one of the potential reactions for the design of selective Hg^{2+} probes. Recently, several Hg^{2+} probes have been synthesized on this basis, where the desulfurization of a thiocarbonyl group of the probe[8] and subsequent structure rearrangement[9] leads to a drastic change in the fluorescence property of the probe. These probes allow selective Hg^{2+} detection in aqueous media, and some of them are applicable to the samples with a relatively broader pH range, 2–9,[9a] 4–9,[8a] 4–10,[9b] and 5–10.[9c]

Coumarin is a dye used extensively due to its excellent photophysical properties such as high fluorescent quantum yield and photostability.[10] In particular, 7-aminocoumarin derivatives show strong fluorescence at a broad pH range (2–12).[11] In the present work, we synthesized a 7-aminocoumarin derivative containing a thiourea moiety (**1**, Scheme 1). The probe **1** allows rapid, selective, and quantitative Hg^{2+} detection in aqueous media with a significantly broader pH range, 2–12. The probe shows strong fluorescence, but the intensity decreases quantitatively with an increase in the Hg^{2+} amount. The Hg^{2+}-promoted fluorescence quenching is due to the decrease in an intramolecular charge transfer (ICT) character of the probe, associated with the desulfurization of the thiocarbonyl moiety.



Scheme 1 Synthesis of the probe, **1**.

Results and discussion

The probe **1** was synthesized by two step reactions, as summarized in Scheme 1 (see the Experimental section). Reaction of 7-amino-4-methylcoumarin with 2-bromoethylamine hydrobromide in 1,4-dioxane at 373 K affords **3** with 94% yield. Reaction of **3** with phenyl isothiocyanate in DMF at 363 K gives rise to the probe **1** as a pale yellow solid with 12% yield. The purity of **1** was fully confirmed by ^1H, ^{13}C NMR and LD-TOF MS analysis.

Fig. 1a shows the fluorescence spectra (λ_{ex} = 363 nm) of the probe **1** (10 μM) measured in a buffered MeCN–water mixture (1/1 v/v; HEPES 100 mM; pH 7.0) with 1 equiv. of respective metal cations. Without cations, **1** shows a strong fluorescence at 390–570 nm, assigned to a coumarin fluorescence, where the fluorescence quantum yield (Φ_F) is determined to be 0.435.[12] Addition of Hg^{2+} leads to a significant decrease in the fluorescence intensity ($\Phi_F < 0.02$). As shown in Fig. 2, a bright blue fluorescence of **1** completely disappears upon Hg^{2+} addition. In contrast, addition of other metal cations to **1** shows almost the same spectra as that obtained without cations, indicating that **1** allows selective fluorescence quenching against Hg^{2+}. It must be noted that the

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† Electronic supplementary information (ESI) available: Supplementary data (Figs. S1–S17) and Cartesian coordinates for compounds. See DOI: 10.1039/b924015b

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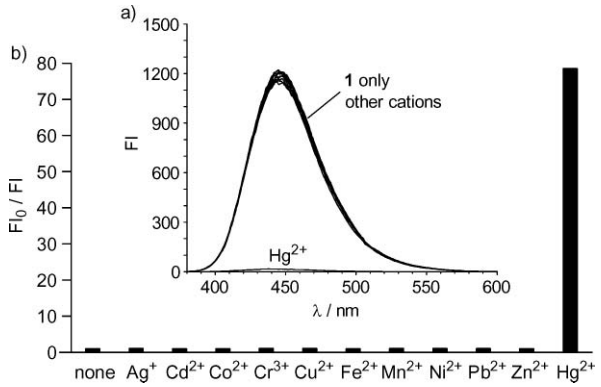

Fig. 1 (a) Fluorescence spectra ($\lambda_{ex} = 363$ nm) of **1** (10 μM) measured in a buffered MeCN–water mixture (1/1 v/v; HEPES 100 mM; pH 7.0) with respective cations (1 equiv.) at 298 K, where perchlorate (Hg^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}), nitrate (Ni^{2+}, Co^{2+}), and tetrafluoroborate salts (Ag^{+}) were used as the cation source. The measurements were performed after stirring the solution for 1 min with cations. (b) The ratio of fluorescence intensity (FI_0/FI) of **1**, where FI_0 and FI are the intensity measured at 445 nm without and with cations.

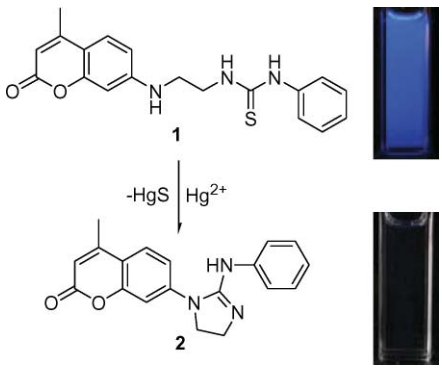

Fig. 2 The proposed mechanism for the fluorescence quenching of **1** upon Hg^{2+} addition, and fluorescence color change of the solution.

fluorescence response of **1** to Hg^{2+} is unaffected by other metal cations (see ESI†, Fig. S1), indicating that **1** detects Hg^{2+} selectively even in the presence of other metal cations. It must also be noted that the fluorescence response occurs within 1 min (see ESI†, Fig. S2), indicating that **1** allows rapid Hg^{2+} detection. In addition, Hg^{2+} salts with different counteranions such as $Hg(ClO_4)_2$, $HgCl_2$, and $Hg(CF_3SO_3)_2$ show almost the same spectral changes of **1** (see ESI†, Fig. S3). This suggests that the counteranion effects are negligibly small.

Fig. 3 shows the result of fluorescence titration of **1** with Hg^{2+} ($\lambda_{ex} = 342$ nm). The stepwise Hg^{2+} addition to **1** leads to a decrease in the fluorescence intensity, where the intensity becomes almost zero upon addition of 1 equiv. of Hg^{2+}. As shown in Fig. 3b, a linear relationship is observed between the fluorescence intensity and the Hg^{2+} amount at the range of 0.02–1 equiv. of Hg^{2+}, which corresponds to 0.2–10 μM Hg^{2+}. This clearly indicates that **1** enables quantitative Hg^{2+} detection at >0.2 μM Hg^{2+} in aqueous media.

Fig. 4 shows the results of absorption titration of **1** with Hg^{2+}. Without cations, **1** shows a distinctive absorption band at 320–420 nm with a maximum absorption at 363 nm. Hg^{2+} addition leads to a decrease in this absorption, along with an increase in

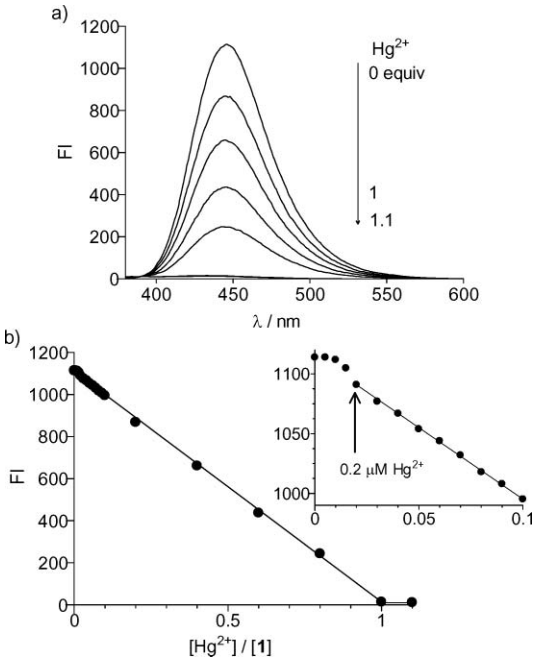

Fig. 3 (a) Change in fluorescence spectra ($\lambda_{ex} = 342$ nm) of **1** (10 μM) measured in a buffered MeCN–water mixture (1/1 v/v; HEPES 100 mM; pH 7.0) upon addition of Hg^{2+}. (b) Change in the fluorescence intensity monitored at 445 nm.

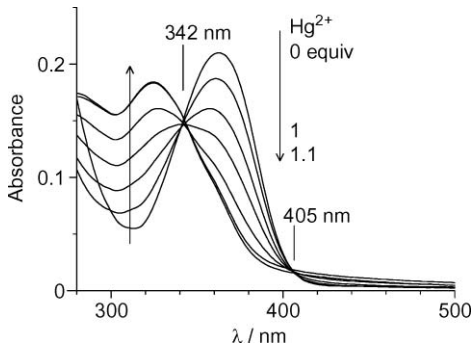

Fig. 4 Change in absorption spectra of **1** (10 μM) measured in a buffered MeCN–water mixture (1/1 v/v; HEPES 100 mM; pH 7.0) upon addition of Hg^{2+}.

325 nm absorption band. The spectral change almost stops upon addition of 1 equiv. of Hg^{2+}, which is similar to the change in fluorescence spectra (Fig. 3). These titration data clearly suggest that **1** associates with Hg^{2+} in a 1 : 1 stoichiometry. The clear isosbestic points at 342 nm and 405 nm in the absorption spectra (Fig. 4) indicate that the reaction of **1** with Hg^{2+} produces a single component. Addition of excess amount of EDTA to the resulting solution does not show further spectral change (see ESI†, Fig. S4), indicating that **1** reacts with Hg^{2+} irreversibly.

As shown in Fig. 2, the fluorescence quenching of **1** upon addition of Hg^{2+} is due to the Hg^{2+}-promoted desulfurization of the thiocarbonyl moiety of **1** followed by cyclization,[13] leading to the formation of an imidazoline derivative, **2**. The formation of **2** is fully confirmed by ^1H, ^{13}C NMR, and FAB MS analysis of the compound obtained by the reaction of **1** and $Hg(ClO_4)_2$ in MeCN at room temperature (see the Experimental section).[14]

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The fluorescence quenching associated with the Hg^{2+}-promoted transformation of **1** to **2** is due to the decrease in an intramolecular charge transfer (ICT) character of the compound. As reported,[15] the excited-state 7-aminocoumarin derivatives have an ICT character and, hence, allows strong fluorescence. The ICT character of the excited-state **1** is confirmed by absorption spectra of **1** measured in different solvents. Fig. 5 shows the relationship between λ_{max} of the absorption spectra and the empirical solvent polarity parameter, E_T^N,[16] of the solvents. The λ_{max} of **1** red-shifts with an increase in the solvent polarity. This indicates that dipole moment of the excited-state **1** is higher than that of the ground state,[17] and the excited-state indeed has an ICT character. The fluorescence spectrum of **1** also red-shifts with an increase in the solvent polarity (see ESI†, Fig. S6). This also supports the ICT character of the excited-state **1**.[17d,18] In contrast, as shown in Fig. 5, λ_{max} of the absorption spectra of the compound **2** shows a minor solvent-dependent shift. This indicates that the ground- and excited-states **2** have similar dipole moments, and the excited-state has a minor ICT character.[19] These findings clearly indicate that the decrease in ICT character of the probe molecule, associated with the transformation from **1** to **2** leads to the fluorescence decrease (Fig. 2).

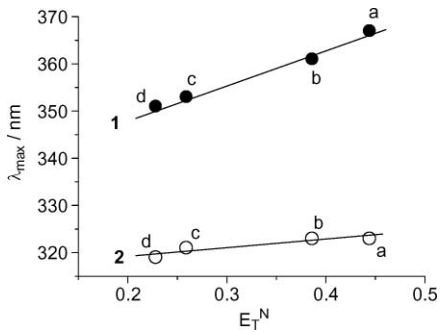

Fig. 5 Relationship between λ_{max} of the absorption spectra of **1** and **2** (10 μM) and the solvent polarity parameter, E_T^N, of the solvents. The solvents are (a) DMSO, (b) DMF, (c) chloroform, and (d) ethyl acetate, respectively. The spectra are shown in Fig. S5 (see ESI†).

As reported,[20] the ICT character of 7-aminocoumarin derivatives depends strongly on conformation of the amine moiety; the amine moiety planar to the benzopyran plane creates an ICT character, while the distortion of the moiety leads to a decrease in ICT character. To clarify the conformation of the amine moiety, *ab initio* molecular orbital calculations were performed with the Gaussian 03 program.[21] Fig. 6a shows the optimized geometry of the compound **1**. The dihedral angle of the C1-N1-H1 plane of the amine moiety to the benzopyran plane is determined to be 17°. In contrast, as shown in Fig. 6b, the C1′-N1′-C2′ plane of the compound **2** has a larger angle (30°), indicating that **2** has a more distorted amine moiety as compared to **1**. The results clearly suggest that the Hg^{2+}-promoted desulfurization of **1** leads to a distortion of the amine moiety; this causes a decrease in ICT character, resulting in fluorescence quenching.

A notable feature of the probe **1** is that it is able to detect Hg^{2+} at a broad pH range. Fig. 7 shows the fluorescence intensity of **1** obtained without and with Hg^{2+} as a function of pH. Without Hg^{2+}, **1** shows a strong fluorescence at a broad pH range 2–12. Upon addition of Hg^{2+}, the intensity decreases to almost zero

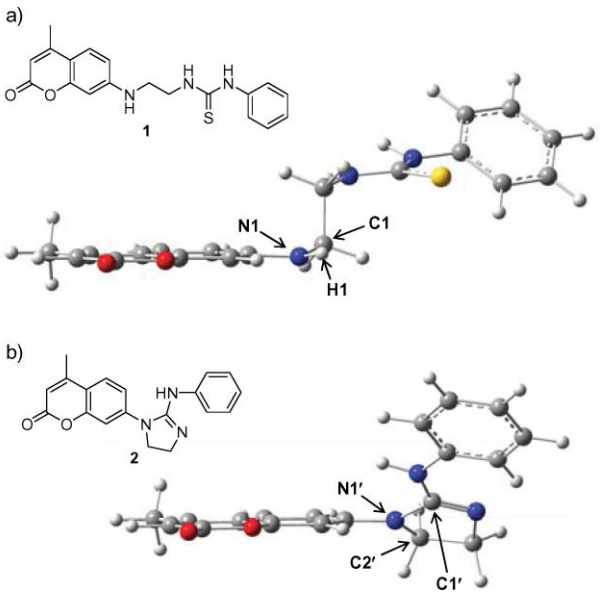

Fig. 6 Calculated structures of (a) **1** and (b) **2** (B3LYP/6-31G*), where the gray, blue, red, yellow, and white atoms denote C, N, O, S, and H atoms, respectively.

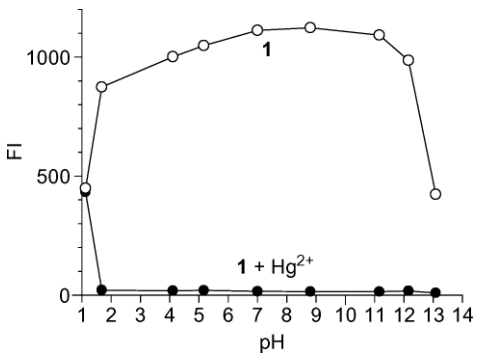

Fig. 7 Change in fluorescence intensity ($\lambda_{ex} = 363$ nm, $\lambda_{em} = 445$ nm) of **1** (10 μM) in a MeCN–water mixture (1/1 v/v) measured with and without Hg^{2+} (1 equiv.) as a function of pH.

at the same region. This indicates that **1** successfully reacts with Hg^{2+} and allows Hg^{2+} detection at a pH range 2–12, which is the broadest among the previously reported Hg^{2+} probes.[6–9]

The sensitivity of **1** is not affected by water content of the sample; as shown in Fig. S7 (see ESI†), Hg^{2+} addition to **1** creates successful fluorescence quenching even in the presence of 20–80% water. In addition, as shown in Fig. S8 (see ESI†), the fluorescence quenching of **1** by Hg^{2+} occurs successfully even in the presence of excess amount of NaCl (100 equiv.). This indicates that **1** allows Hg^{2+} detection for samples with high salt concentration.

Conclusions

We found that a coumarin–thiourea conjugate (**1**) behaves as a fluorescent probe for selective Hg^{2+} detection in aqueous media with a broad pH range 2–12. The selective fluorescence response of **1** is due to the Hg^{2+}-promoted desulfurization of the thiocarbonyl moiety, leading to a decrease in ICT character of the excited state coumarin moiety. The molecular design presented here may

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contribute to the development of more efficient and more useful Hg^{2+} probes in aqueous media.

Experimental

General

Apparatus and instruments were described elsewhere.[22] The spectral measurements were carried out with a 10-mm path length quartz cell under aerated conditions. LD-TOF MS chart was obtained with a Shimadzu/Kratos AXIMA-CFR spectrometer.[23]

Synthesis

Compound 3. 7-Amino-4-methylcoumarin (0.18 g, 1.0 mmol) and 2-bromoethylamine hydrobromide (0.11 g, 0.54 mmol) were refluxed in 1,4-dioxane (3 mL) for 12 h. The resultant was concentrated by evaporation. Ethyl acetate was added to the residue, and the solution was extracted with water (200 mL × 2). The combined aqueous solution was washed with ethyl acetate, concentrated by evaporation, and dried *in vacuo*, affording **3** as a pale orange solid (108.2 mg, 92%). ^{1}H NMR (D_2O, 270 MHz, TMS): δ (ppm) = 7.45 (d, J = 8.90 Hz, 1H), 6.70 (d, J = 8.90 Hz, 1H), 6.48 (s, 1H), 5.97 (s, 1H), 3.57 (t, J = 6.02 Hz, 2H), 3.30 (t, J = 6.02 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (DMSO-d_6, 68 MHz, TMS): δ (ppm) = 160.2, 155.2, 153.3, 151.4, 125.8, 110.3, 109.1, 107.8, 96.5, 37.6, 28.9, 17.9. EI MS: Calcd for $C_{12}H_{14}N_2O_2$: 218.3, found: m/z 218.1 (M^+). HRMS (EI$^+$) m/z calcd for $C_{12}H_{14}N_2O_2$ [M^+] 218.1055, found 218.1067. ^{1}H, ^{13}C NMR and EI MS charts are shown in Figs. S9–S11 (see ESI†).

Compound 1. **3** (0.25 g, 1.1 mmol) and phenyl isothiocyanate (0.50 mL, 4.2 mmol) were stirred in DMF (6 mL) at 363 K for 24 h. The resultant was concentrated by evaporation. Water was added to the residue, and the resulting aqueous phase was extracted with ethyl acetate (200 mL × 2). The combined organic layer was washed with water, dried over Na_2SO_4, and concentrated by evaporation. The crude product was purified by silica gel column chromatography with CH_2Cl_2–ethyl acetate (20/1 v/v) and CH_2Cl_2–ethyl acetate (1/1 v/v). The latter eluent was concentrated by evaporation and dried *in vacuo*, affording **1** as a pale yellow solid (47.8 mg, 12%). ^{1}H NMR (CD_3CN, 270 Mz, TMS): δ (ppm) = 8.11 (br, 1H), 7.42 (d, J = 8.57 Hz, 1H), 7.33–7.39 (m, 2H), 7.20–7.24 (m, 3H), 6.71 (br, 1H), 6.60 (dd, J = 2.30 Hz, 6.43 Hz, 1H), 6.52 (d, J = 2.31 Hz, 1H), 5.89 (d, J = 1.15 Hz, 1H), 5.41 (br, 1H), 3.77 (q, J = 6.15 Hz, 2H), 3.40 (q, J = 6.15 Hz, 2H), 2.33 (d, J = 1.16 Hz, 3H). ^{13}C NMR (DMSO-d_6, 68 MHz, TMS): δ (ppm) = 180.1, 160.3, 155.4, 153.3, 152.1, 138.5, 128.4, 125.6, 124.1, 123.1, 110.0, 108.6, 107.3, 96.2, 42.7, 41.2, 17.9. MS (LD-TOF): Calcd for $C_{19}H_{19}N_3O_2S$: 353.4, found: m/z 375.8 (M^+ + Na). Elemental anal.: Calcd for $C_{19}H_{19}N_3O_2S$: C, 64.57; H, 5.42; N, 11.89; Found: C, 64.34; H, 5.22; N, 11.69. ^{1}H, ^{13}C NMR, and LD-TOF MS charts are shown in Figs. S12–S14 (see ESI†).

Compound 2. $Hg(ClO_4)_2{\cdot}6H_2O$ (129.0 mg, 0.25 mmol), **1** (82.1 mg, 0.23 mmol), and triethylamine (79.7 mg, 0.79 mmol) were stirred in MeCN (20 mL) for 15 min at room temperature. The solid formed was removed by filtration. The solution was concentrated by evaporation. The product was purified by silica gel column chromatography with CH_2Cl_2–ethyl acetate (2/1 v/v). The eluent was dried *in vacuo*, affording **2** as a white solid (48.7 mg, 66%). ^{1}H NMR (CD_3CN, 270 MHz, TMS): δ (ppm) = 7.87 (d, J = 8.41 Hz, 1H), 7.37–7.53 (m, 5H), 7.28–7.32 (m, 2H), 6.34 (q, J = 1.21 Hz,1H), 4.21–4.27 (m, 2H), 3.75–3.82 (m, 2H), 2.46 (d, J = 1.32 Hz, 3H). ^{13}C NMR (DMSO-d_6, 68 MHz, TMS): δ (ppm) = 159.1, 154.8, 153.1, 152.4, 139.4, 135.5, 129.3, 126.7, 126.4, 124.3, 120.1, 118.1, 114.0, 112.4, 50.8, 40.9, 18.0. FAB MS: Calcd for $C_{19}H_{17}N_3O_2$: 319.4, found: m/z 320.3 ($M+H^+$). HRMS (FAB^+) m/z calcd for $C_{19}H_{18}N_3O_2$ [$M+H^+$] 320.1399, found 320.1381. ^{1}H, ^{13}C NMR and FAB MS charts are shown in Figs. S15–S17 (see ESI†).

Computational details

Preliminary geometry optimization was performed using the WinMOPAC version 3.0 software (Fujitsu Inc.) at the semiempirical PM3 level.[24] The obtained structures were fully refined at the DFT level with the Gaussian 03 package,[21] using the B3LYP/6-31+G* basis set for all atoms. Cartesian coordinates for **1** and **2** are shown in ESI†.

Acknowledgements

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