

Ag(I) induced emission with azines having donor–acceptor–donor chromophore†

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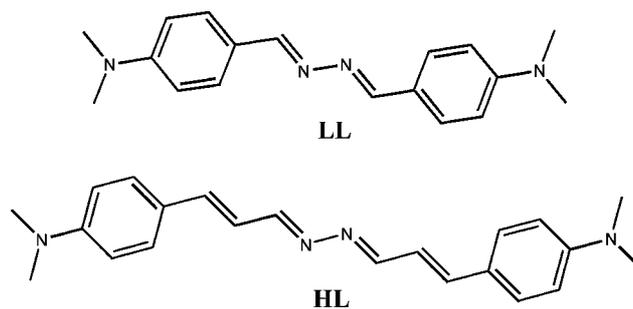
Two azine molecules, [3-{4-(dimethylamino)phenyl}prop-2-en-1-ylidene]hydrazone (**HL**) and [4-(dimethylamino)benzylidene]hydrazone (**LL**) synthesized *via* Schiff base condensation, show an absorption band due to intra-ligand charge transfer (ILCT). Both ligands show weak emission in the absence of a metal ion as input. When Ag⁺ ions are added to either compound in THF, the metal ion gets bonded to the azine moiety resulting in a high intensity emission (~400 fold). While Cu⁺ shows a slight enhancement of emission, other first-row transition, alkali or alkaline-earth metal ions do not show any emission allowing Ag⁺ ions to be detected in the presence of these metal ions. Both the Ag⁺ complexes were characterised by X-ray crystallography and show solid-state spectra similar to their solution spectra. Time-resolved fluorescence measurements done on the complexes show two excited-state lifetimes.

Introduction

Fluorescent chemosensors that exhibit high selectivity and sensitivity for heavy metal ions are currently in great demand for environmental and biological applications.^{1,2} However, fluorescence sensing of a particular metal ion in the presence of a number of others is a challenging problem. This is more so in the case of heavy and transition metal ions as they effectively quench fluorescence through spin–orbit coupling or energy/electron transfer processes.³

Silver (Ag⁺) has received considerable attention because of its antimicrobial activities.⁴ Several possible roles of Ag⁺ in biological systems have been proposed that include interaction and inactivation of vital enzymes,⁵ binding to DNA,⁶ interaction with cell membrane⁷ and interference with the electron transport processes.⁸ Silver and its compounds are widely used in the electrical, photographic and imaging industries, and in pharmaceuticals. Because of the flourishing demand of silver compounds in miscellaneous commercial sectors, severe contamination of the environment by Ag⁺ ions is rising from industrial sludge.⁹ Several reports on bio-accumulation and toxicity of the metal have been reported.¹⁰ Hence, development of sensitive and selective methods for the determination of Ag⁺ ions in trace amounts in various media is of considerable importance. Few fluorescent systems are reported that show emission enhancement/quenching in the presence of Ag⁺ ions.^{11,12} However, the ubiquitous nature of emission quenching reduces its practical utility and hence systems with emission enhancement rather than quenching should be the choice for sensor design.

Herein, two simple azine compounds (**HL** and **LL**), each having a putative cation-binding site in the middle flanked by two electron-donating 4-dimethylaminophenyl moieties (Scheme 1) are presented. Each ligand is poorly emissive in nature but exhibit high intensity emission in the presence of Ag⁺ ions. Other heavy metal ions such as mercury, lead and thallium or, alkali and alkaline-earth metal ions do not show any fluorescence with either ligand. Among the transition metals studied, only Cu⁺ gives a low fluorescence.



Scheme 1 Schematic representation of the ligands.

Results and discussion

The azine compounds, **HL** and **LL** are easily synthesized in high yields from easily available and cheap chemicals. Once isolated, they are found to be stable in air and soluble in common organic solvents. Both ligands afforded single crystals with Ag⁺ salts suitable for X-ray crystallographic analysis.^{13,14}

Electronic spectroscopy

The ligand **HL**, in THF, shows an absorption peak centered on 428 nm, which is attributed^{1b} to an ILCT transition. For **LL**, the ILCT band appears at 384 nm (Fig. 1). When a metal ion is added to either ligand, it binds to the azine group enhancing its acceptor

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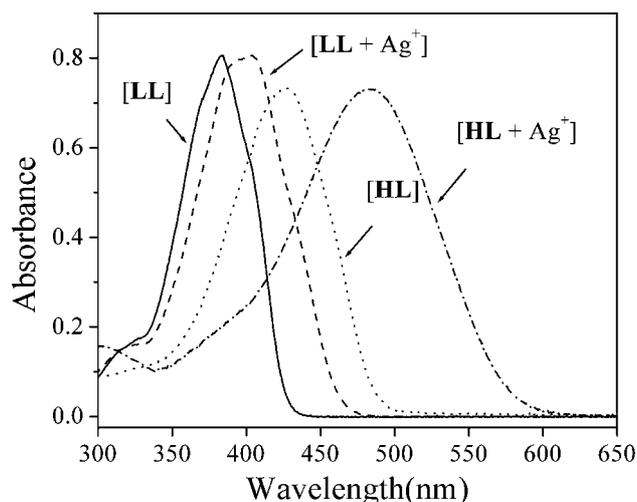


Fig. 1 UV-vis spectra of each ligand (8 μM) in the presence of Ag^+ (40 μM) as the trifluoromethanesulfonate salt in dry THF solvent.

character. This causes a red-shift of this band. The extent of the red-shift (Table 1) depends upon the nature of the metal ion as well as the ligand. Titration of **HL** with Ag^+ in THF gives a well-defined isosbestic point at 445 nm (Fig. 2a) and affords an overall binding constant ($\log\beta$) of 10.54. In case of **LL**, the red-shift of the ILCT band in the presence of Ag^+ ions is less. In this case, $\log\beta$ (Table 1) is determined to be 10.32 from the emission data.¹⁵

Metal-free ligands show very weak emission at 500 and 425 nm for **HL** and **LL**, respectively. We have measured the emission of **HL** in different solvents and it shows weak solvatochromic properties.¹³ Emission responses of the ligands in the presence of different metal ions are investigated with $\sim 10^{-6}$ M solution in freshly purified THF. Among the metal ions studied, Ag^+ ions give high enhancement of emission and Cu^+ ions afford very low enhancement (Fig. 2b). The emission enhancement is due to photo-induced charge transfer (ICT) process operating in presence of the metal ion.^{1b} In each case, the enhancement remains intact when metal ions other than Fe^{+2} , Co^{+2} , Cu^{+2} , Hg^{+2} are added. In the case of **LL**, only Fe^{+2} while for **HL** all four metal ions quenched the fluorescence due to Ag^+ . In a DMF–water mixture (1 : 1 v/v), the enhancement reduces to 40% with respect to the value observed¹³ with pure DMF. However, this lowering may be due to poor stability of the ligand in water. As the polarity of THF is different from that of DMF, position of the emission band differs in the two

Table 1 Spectroscopic data for **LL** and **HL** and their $\text{Ag}(\text{t})$ complexes in THF

Compound	$\lambda_{\text{abs}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}^a$	Quantum yield (ϕ) ^b	$\log\beta$	τ/ps^c
LL	384	425	0.00012	—	—
HL	428	500	0.00016	—	—
LL + 2 Ag^+	400	487	0.038	10.32	3.36, 34.74
LL + 2 Cu^+	404	508	0.0012	—	—
HL + 2 Ag^+	470	560	0.046	10.54	3.9, 401
HL + 2 Cu^+	484	581	0.0022	—	—

^a Excitation wavelength were 384 nm (**LL**) and 445 nm (**HL**). ^b Fluorescence maxima were obtained by taking [**LL**] and [**HL**] = 1 μM ; [M^{n+}] = 20 μM . The quantum yield (ϕ) is calculated by taking standard quinine sulfate in 1 N H_2SO_4 ($\phi = 0.54$). The error in ϕ is 15% for free ligands, otherwise 10% in each case. ^c Lifetime data is in ps.

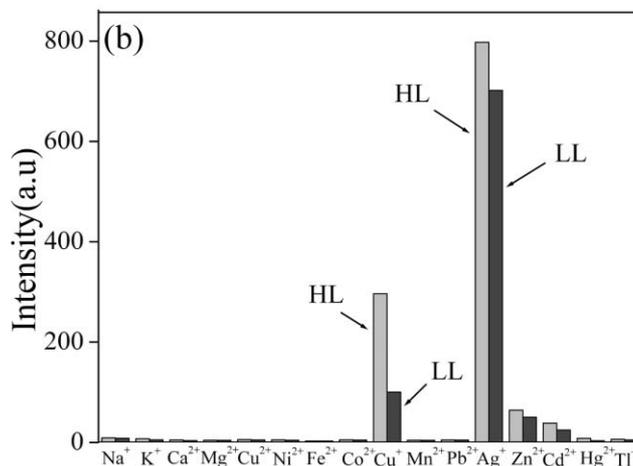
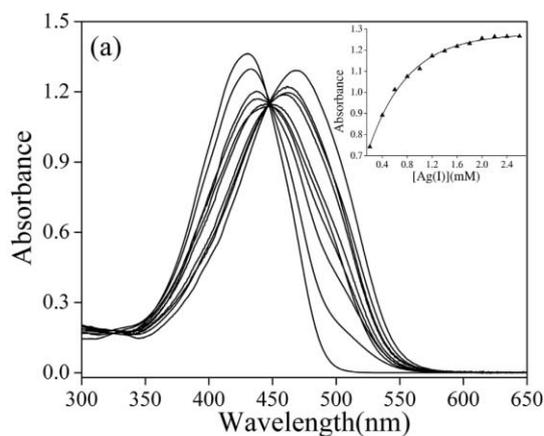


Fig. 2 (a) UV-vis spectral changes observed for **HL** upon addition of Ag^+ as the triflate salt in THF at 298 K. [**HL**] = 0.01 mM; [Ag^+] = (0.02 mM). Inset represents the variation in absorbance of a solution of **HL** (0.01 mM) in THF as a function of [Ag^+]. (b) Emission response of **HL** (2 μM) and **LL** (2 μM) in the presence of [Ag^+] (40 μM) in dry THF. Dark grey for **LL** and light grey for **HL**.

solvents although its nature remains unaltered (Fig. S2.9).[†] The detection limit for Ag^+ in the DMF–water mixture (1 : 1 v/v) is 2 mM and this response is linear up to 15 mM Ag^+ concentration. Therefore, Ag^+ can be detected within the environment, albeit with a poor detection limit.

A report is available in the literature¹⁴ that shows **LL** to be emissive in a mixed ethanol + DCM + DMF solvent at 10^{-4} M concentration and its emission is completely quenched in presence of AgNO_3 . We are unable to reproduce this result and find that in the solvent system at the concentration mentioned, addition of AgNO_3 actually showed large emission enhancement.¹³ Titration of **HL** and **LL** with Ag^+ in THF, gradual emission enhancements with red-shift of emission wavelengths are observed (Fig. 3). Maximum emission intensity is observed on adding 2 equiv. of Ag^+ to **HL**. Other solvents like DMF and MeCN exhibit similar results.

The solid-state structures^{13,14} of the Ag -complexes reveal that in each case, one Ag^+ ion is bonded to one N of the azine moiety on each side. In $[\text{Ag}_2(\text{HL})(\text{DMF})_2(\text{H}_2\text{O})_2]$ (**I**), each metal is also bonded to one water and one DMF giving it tri-coordination (Fig. 4). Each metal also shows weak bonding interactions¹⁶ with

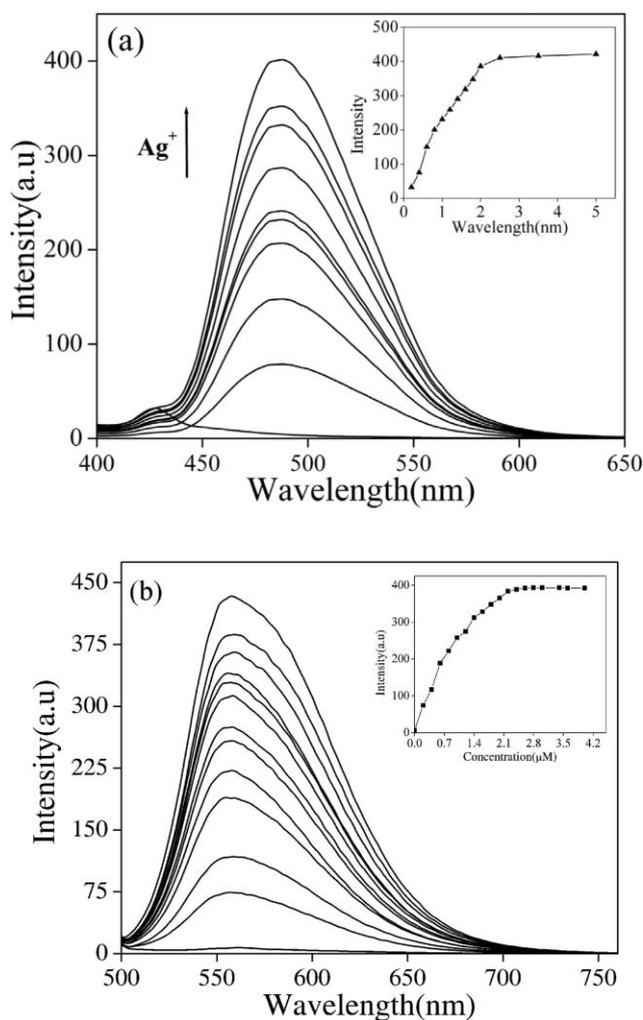


Fig. 3 (a) Emission intensity response of LL (2 μM , THF) upon addition of increasing amount of Ag^+ ions (0–2.2 μM). Excitation wavelength was 384 nm. (b) Emission intensity response of HL (2 μM , THF) upon addition of increasing amount of Ag^+ ions (0–2.2 μM). Inset: emission change at 560 nm with increasing concentrations of Ag^+ ion. Excitation wavelength was 445 nm.

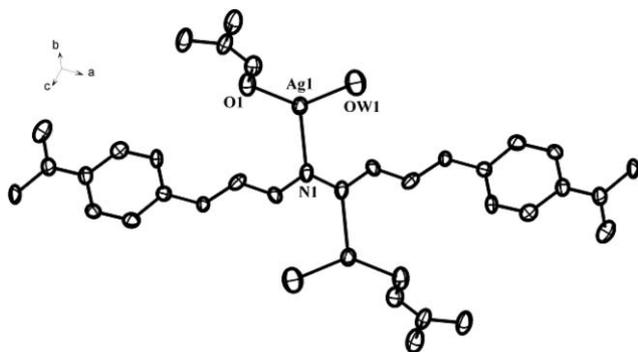


Fig. 4 X-Ray structure of the Ag^+ complex with HL ligand. H atoms and anions are omitted for clarity. The atoms are drawn as thermal ellipsoids at the 50% probability level. Selected bond distances (\AA) and angles ($^\circ$) are: Ag1–N1 2.277(7), Ag1–O1 2.326(6), Ag1–OW1 2.328(7), N1–Ag1–O1 118.5(2), N1–Ag1–OW1 109.6(3), O1–Ag1–OW1 100.8(2). Structural information for **2** is given in the ESI.†

two C atoms of benzene (η^2 -mode) of a neighbouring ligand¹³ All Ag–O and Ag–N bond distances are normal within statistical errors.¹⁷

In $\{[\text{Ag}_2(\text{LL})_3(\text{NO}_3)_2] \cdot (\text{H}_2\text{O})\}$, (**2**) each Ag^+ ion shows^{13,14} a distorted tetrahedral geometry with bonding from two O atoms of one NO_3^- anion and two azine N atoms from two LL units. All Ag–O and Ag–N bond distances are within normal ranges.¹⁷ Both **1** and **2** show emission in the solid-state at 293 K as well.¹³

When crystals of **1** are dissolved in THF, the emission band¹³ observed is almost identical to that obtained by adding Ag^+ ions to the ligand solution in THF. Similarly, crystals of **2** dissolved in DMF, exhibit an emission band¹³ identical to the one obtained by adding Ag^+ ions to the ligand solution in DMF. To show reversibility, **1** dissolved in THF is treated with 2 equiv. of Bu_4NCl salt when the emission intensity drastically reduces to the level of metal-free ligand. Upon addition of 2 equiv. of $\text{Ag}(\text{CF}_3\text{SO}_3)$, the emission intensity band¹³ is restored almost to the initial value. We have repeated this process five times.

Time-resolved fluorescence decay processes of both the ligand in presence of Ag^+ ions are measured by femtosecond fluorescence up-conversion setup. Both the complexes show bi-exponential decay processes with two positive factors (Fig. S4.1 and S4.2).† The study reveals an ultra-fast 4 ps component for both the complexes, while 400 and 35 ps slow components are observed for HL and LL complexes with Ag^+ ions, respectively. Two decay components are due to ILCT¹⁸ and photo-isomerisation¹⁹ lifetimes. This can be easily ascribed to the fact that on performing solvent variation studies on ligand alone shows appearance of emission band with polar protic solvents. It is well known that polar solvents stabilize the charge separated species. It is further observed that in highly viscous solvents like ethane-diol there is substantial enhancement in emission intensity suggesting that intramolecular rotation is hindered. The faster component has been assigned to ICT because in most of the molecules the electronic rearrangement can occur much faster than isomerisation.

Conclusion

In conclusion, we have designed very simple molecules that are capable of showing Ag^+ ions sensitive fluorescence. This sensing ability of a fluorescent signalling system is of enormous importance in biomedical research. We are presently working on other acyclic receptors with structural variations to understand how heavy and paramagnetic transition metal ions, which are known quenchers, can selectively cause fluorescence enhancement.

Experimental

Materials

All reagent-grade chemicals were used without purification unless otherwise specified. Silver trifluoromethanesulfonate, perchlorate salts of all the other metal ions, 4-(dimethylamino)benzaldehyde and 4-(dimethylamino)cinnamaldehyde were purchased from Aldrich. 80% hydrazine hydrate was obtained from S. D. Fine Chemicals (India). Solvents were received from S. D. Fine Chemicals (India) and they were purified prior to use. The syntheses of

the compounds (Scheme 1) were achieved by simple Schiff base condensation.

Physical measurements

¹H-NMR spectra were recorded on a JEOL JNM-LA400 FT (400 MHz) instrument in CDCl₃. ESI mass spectra were recorded on a MICROMASS QUATTRO II triple quadrupole mass spectrometer. The ESI capillary was set at 2.42 kV and the cone voltage was 40 V. Melting points were determined with an electrical melting point apparatus by PERFIT, India and were uncorrected. UV-vis spectra were recorded on a JASCO V-570 spectrophotometer at 293 K and the average of three measurements were taken. The deviations in molar absorption coefficients were in the last digit only. Steady-state fluorescence spectra were obtained using a Perkin-Elmer LS 50B Luminescence spectrometer at 293 K with excitation and emission band-pass 5 nm. The decays were measured by femtosecond fluorescence up-conversion setup, made by Spectra Physics, using Ti : sapphire laser as the source operating at 80 MHz frequency. The decays were analysed²⁰ by a user-defined program by igorpro software. The FWHM of the pulse is ~100 fs per 10 nm. The solid-state emission and excitation spectra were recorded by using a commercial spectrometer (SPEX, Fluorolog 3, Model FL3–22). The excitation light, from a 450 W xenon lamp having a spot size dimension of ~1 mm × 12 mm, was incident on the sample kept in quartz cuvette with a path length of 10 mm at 293 K. All the fluorescence spectra were collected at 22.5° from the direction of the incident excitation light to minimize the specular reflection from the surface. The band pass for the excitation and emission monochromators was kept as 2 nm. The integration time was kept 0.2 second and the emission monochromator stepped through 1 mm while recording the spectra. Fluorescence quantum yields in each case were determined by comparing the corrected spectrum with that of standard quinine sulfate²¹ ($\phi = 0.54$ in 1 N H₂SO₄), taking the area under the total emission. The fluorescence measurements in solutions were carried out at ~2 × 10⁻⁶ M concentration unless otherwise specified. The complex stability constant K_a was determined¹⁵ from the change in absorbance or fluorescence intensity resulting from the titration of dilute solutions (~10⁻⁵–10⁻⁶ M) of ligand against metal ion concentration. The reported values gave good correlation coefficients (≥0.99).

X-Ray structural studies

Single-crystal X-ray data were collected at 293 K on a Bruker SMART APEX CCD diffractometer using graphite monochromated MoK α radiation ($\lambda = 0.71073$ Å). The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from the International Tables for X-Ray Crystallography. The data integration and reduction were processed with SAINT software.²² The structure was solved by the direct method using SHELXTL and was refined on F^2 by full-matrix least-squares technique using SHELXL-97.²³ All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in successive difference Fourier maps and they were treated as riding atoms using SHELXL default parameters. For complex **2**, the H atoms attached to water O could not be located

Table 2 Crystal data and structure refinement for LL·HPF₆ and **1**

	LL·HPF ₆	1
Empirical formula	C ₃₈ H ₄₆ N ₈ OF ₁₂ P ₂	C ₁₅ H ₂₂ N ₃ O ₅ F ₃ SAg
FW	920.77	521.29
T/K	100	293
Radiation	MoK α	MoK α
$\lambda/\text{Å}$	0.71069	0.71069
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
$a/\text{Å}$	9.634(5)	8.762(5)
$b/\text{Å}$	11.077(5)	10.555(5)
$c/\text{Å}$	11.728(5)	12.204(5)
$\alpha/^\circ$	64.345(5)	100.934(5)
$\beta/^\circ$	79.578(5)	100.595(5)
$\gamma/^\circ$	66.542(5)	107.276(5)
$V/\text{Å}^3$	1034.9(8)	1022.9(9)
Z	1	2
$\rho_{\text{calcd}}/\text{Mg m}^{-3}$	1.477	1.693
μ/mm^{-1}	0.202	1.145
$F(000)$	476	526
Reflections collected	4928	4883
Independent reflections	2640	3982
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
GOF	1.088	1.126
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0813$ $wR_2 = 0.2122$	$R_1 = 0.0650$ $wR_2 = 0.1414$
R indices (all data)	$R_1 = 0.1465$ $wR_2 = 0.3057$	$R_1 = 0.0959$ $wR_2 = 0.2081$
R_{int}	0.0319	0.0274

in the difference maps.¹⁵ The crystal data for two structures are given in Table 2.

Syntheses

Compound LL. In 40 mL absolute ethanol, 0.4 g of 80% hydrazine hydrate (1 mmol) and 2.5 g of 4-(dimethylamino)-benzaldehyde (2.1 mmol) were added in a 100 mL round-bottomed flask. The reaction mixture was stirred at room temperature overnight. A yellow precipitate that formed was filtered and washed with ethanol (4 × 20 mL). After drying in vacuum, the product was obtained as a yellow solid (4 g, 81% yield). Mp: 235 °C. $\nu_{\text{max}}/\text{cm}^{-1}$ 1519 (CN). δ_{H} (CDCl₃, 400 MHz) 3.01 (s, 12 H, CH₃), 6.69 (d, 4 H, $J = 9.0$ Hz, H_{ar}), 7.69 (d, 4 H, $J = 8.7$ Hz, H_{ar}), 8.56 (s, 2 H, N=CH). m/z 295.19 (LL, 100%) (ESI). Anal. calcd for C₁₈H₂₂N₄ found: C 73.3, H 7.6, N 19.1% and requires: C 73.4, H 7.5, N 19.0%. This was further crystallized as the protonated form where hexafluorophosphate plays the role of the anion (LL·HPF₆).

Compound HL. This compound was synthesized as described in the above procedure taking 4-(dimethylamino)cinnamaldehyde in place of 4-(dimethylamino)benzaldehyde. The compound was isolated as an orange solid (0.61 g, 86% yield). Mp: 240 °C. $\nu_{\text{max}}/\text{cm}^{-1}$ 1595 (CN). δ_{H} (CDCl₃, 400 MHz) 3.01 (s, 12 H, CH₃), 6.66 (d, 4 H, $J = 9.0$ Hz, H_{ar}), 6.88 (dd, 2 H, $J = 9.6, 15.7$ Hz, vinylic), 6.98 (d, 2 H, $J = 15.8$ Hz, vinylic), 7.39 (d, 4 H, $J = 8.7$ Hz, H_{ar}), 8.32 (d, 2 H, $J = 9.5$ Hz, N=CH). m/z 347.22 (HL, 100%) (ESI). Anal. calcd for C₂₂H₂₆N₄ found: C 76.1, H 7.6, N 16.2% and requires: C 76.2, H 7.5, N 16.1%.

Compound $\{[\text{Ag}(\text{C}_{11}\text{H}_{13}\text{N}_2)(\text{DMF})(\text{H}_2\text{O})] \cdot (\text{O}_3\text{SCF}_3)\}_n$ (**1**). Ag(O₃SCF₃) (0.49 g, 1.92 mmol) was dissolved in DMF (1.5 mL) and added to a solution of HL (0.84 g, 2 mmol) in DMF (1.5 mL)

at room temperature with stirring. The solution immediately turned deep red. It was filtered and diffused with dry benzene and allowed to evaporate at room temperature. Dark red X-ray quality rectangular-shaped crystals of **1** appeared in about one day. Yield ~ 50%. Anal. calcd for $C_{15}H_{22}F_3N_3O_5SAg$ found: C 34.4, H 4.3, N 8.1% and requires: C 34.5, H 4.2, N 8.0%. m/z 455.12 ($[HL + Ag]^+$, 100%) and 562.21 ($[HL + 2Ag]^+$, 50%) (ESI).

Compound $\{[Ag_2(LL)_3(NO_3)_2] \cdot (H_2O)\}$ (**2**). This complex was synthesized following a reported procedure.¹⁴ Anal. calcd for $C_{54}H_{68}Ag_2N_{14}O_7$ found C 52.6, H 5.8, N 15.6% and requires C 52.3, H 5.5, N 15.8%. m/z 401.08 ($[LL + Ag]^+$, 95%) and 501.03 ($[LL + 2Ag]^+$, 45%) (ESI).

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