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A Luminescent Silver(I) Carbene Stair Polymer

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1-(9-Anthracenylmethyl)-3-ethylimidazolium iodide was heated in CH_2Cl_2 solution with silver oxide to afford a stair polymer of N-heterocyclic carbene silver(I), which gave strong anthracene-type fluorescence. The carbene moiety could be displaced from this polymer by pyridine to afford a known polymer with a similar shape but a tighter framework; this polymer showed an emission band at 579 nm arising from a Ag−Ag interaction.

Introduction

N-Substituted imidazol-2-ylidenes (imy)[1] are stable enough to be isolated in their free state. Since their discovery, the application of imidazol-2-ylidenes as ligands in metal complexes has attracted considerable attention. Interest in this class of carbenes and their derivatives has kept growing in the past decade owing to the inherent stability of its members,[2] unusual characteristics of structure and bonding,[3] and more importantly, their potential applications in synthesis and catalysis in organic reactions[4] and materials.[5] These carbenes obviously behave primarily as a donor ligand (i.e., a Lewis base) without significant back-donation. Among them, examples of N-heterocyclic carbene silver(I) complexes have been reported,[6] but few polymers have been described.[7] Herein we report the synthesis, structure, reaction, and photophysical properties of a silver(I)−imy stair polymer, poly[1-(9-anthracenylmethyl)-3-ethylimidazol-2-ylidene silver iodide], which luminesces strongly.

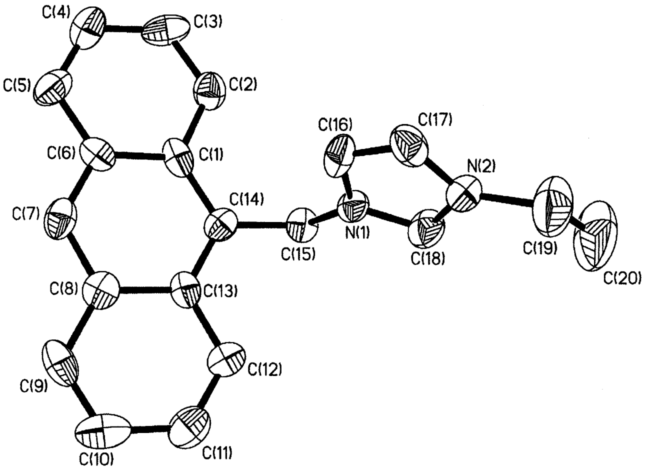

Figure 1. Perspective view of the cation in **1** and anisotropic displacement parameters depicting 30% probability. Hydrogen atoms have been omitted for clarity.

Results and Discussion

Imidazole was alkylated with 9-(chloromethyl)anthracene to give a yellow powder of 1-(9-anthracenylmethyl)imidazole, which was further alkylated with ethyl iodide in analogy to a reported process[8] to give a yellow powder of 1-(9-anthracenylmethyl)-3-ethylimidazolium iodide (**1**) (Scheme 1). Yellow crystals of 1-(9-anthracenylmethyl)-3-ethylimidazolium iodide suitable for X-ray diffraction were obtained by recrystallization from CH_2Cl_2/acetone, and its molecular structure is shown in Figure 1. Precursor **1** is stable to air and moisture, soluble in polar organic solvents such as dichloromethane, acetonitrile, and methanol, scarcely soluble in THF and benzene, and insoluble in diethyl ether and petroleum ether.

Stair polymer **2** was prepared by the reaction of imidazolium iodide **1** and silver oxide ($^1/_2$ mol equiv) in

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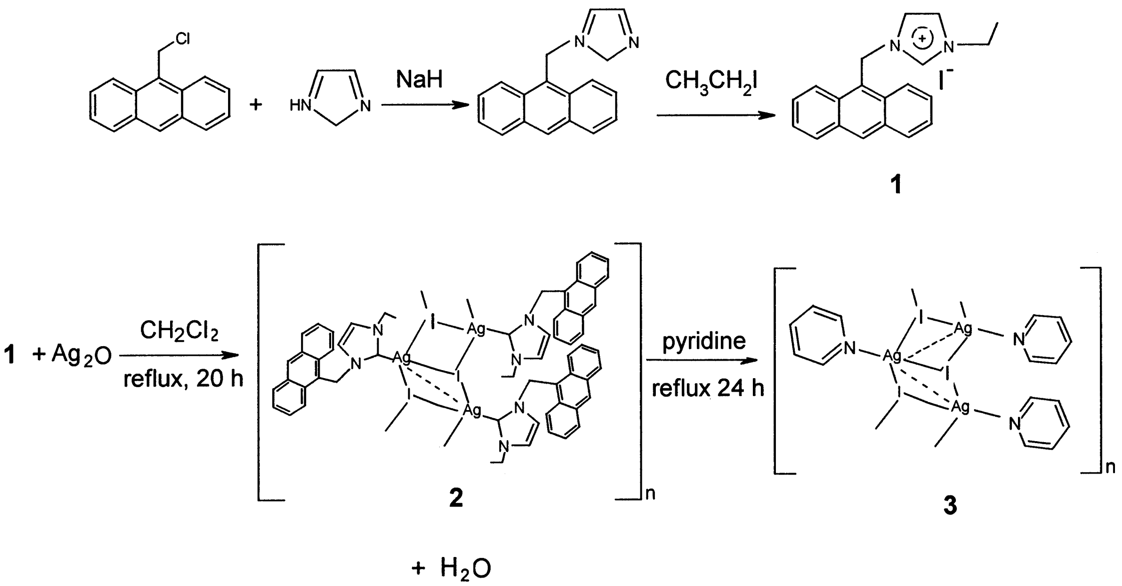
Scheme 1



refluxing dichloromethane (Scheme 1). Polymer **2** was obtained as a yellow powder from dichloromethane solution in 50% yield and was characterized by elemental analysis and spectroscopic methods. Although polymer **2** is obtained from dichloromethane solution, it was poorly soluble in dichloromethane once it was isolated, which indicates that a building block, probably a dimeric unit of [Imy-AgI]$_2$, was formed as the initial soluble entity which gradually assembled to give **2**. Polymer **2** was stable to air and moisture, moderately light-sensitive, and poorly soluble in CHCl$_3$ and DMSO.

The ^{1}H NMR spectrum of polymer **2** showed no signal in the vicinity of 9.0 ppm, where the imidazolium C$_2$−H signal of **1** was found. It also showed the C$_{4(5)}$−H resonance of the imidazole ring at low field, 7.4−7.5 ppm, indicating substantial electron delocalization in the ring.[6a] In the ^{13}C NMR (DMSO-d_6) spectrum at room temperature, the signal for the C$_2$ atom appears at 179.5 ppm, which is characteristic for a metal carbene signal.[6]

The silver imidazol-2-ylidene polymeric stair structure in **2** was further demonstrated by X-ray analysis. Crystals of **2** suitable for an X-ray diffraction study were obtained at 4 °C from its solution in dichloromethane; 0.5 CH$_2$Cl$_2$ and 0.5 H$_2$O molecules were found to be incorporated in single crystals of polymer **2**. The 0.5 H$_2$O is the water produced in the reaction (Scheme 1). A perspective view of the packing of the polymeric chain is shown in Figure 2. Each silver atom is coordinated by a carbene carbon and three iodine atoms and possesses a distorted-tetrahedral configuration. In contrast, each iodine atom is bound to three silver atoms and exhibits a trigonal-pyramidal arrangement. The Ag(1A)−I(1AA)−Ag(1B)−I(1A) atoms lie in the same plane (maximum deviation 0.0001 Å). The Ag(1A)−Ag(1B) distance is 3.473 Å. The Ag(1A) and I(1AA) atoms with Ag(1D) and I(1B) atoms form another plane, and the Ag(1A) and Ag(1D) distance is 4.063 Å. The dihedral angle of the two planes is 105.9°, and the dihedral angle between the planes consisting of Ag(1A)−I(1AA)−Ag(1B)−I(1A) and Ag(1C)−I(1AB)−Ag(1D)−I(1B) is zero. The C−Ag distance of 2.182 Å is somewhat longer than those of known silver carbene complexes (2.052−2.090 Å),[6] which agrees with the conclusion that the Ag−imy bond shows no π-back-donation and that metal−imy complexes show no metal−carbene double-bond reactivity.[3]

The X-ray crystal packing pattern (Figure 2b) showed an orderly parallel stacking for imidazole as well as for anthracene rings, with respect to themselves, in both sides of the main framework in **2**. In the neatly stacked rings as in Figure 2b, it is significant that the calculated distances of the parallel planes for both types of rings were the same at 3.572 Å. As the center-to-center distance of the anthracene rings is estimated to be 4.570 Å, a π,π-stacking interaction is expected.[9]

In dichloromethane **2** showed anthracene fluorescence similar to but stronger than that of **1**. This can be attributed to the electron-withdrawing effect of silver(I), which inhibits the photoinduced electron transfer (PET) process from the nitrogen atom to the anthracene ring.[10] A broad anthracene excimer emission occurs at 515 nm (Figure 3).

A suspension of polymer **2** in pyridine was heated to give another pale yellow polymer **3** (Figure 4), which was identified by X-ray analysis; it has a structure identical with that prepared previously by the reaction of silver iodide with pyridine.[11] Thus, the carbene moiety was displaced by pyridine, but the fate of the carbene moiety has not been clarified as yet. Crystals of **3** suitable for an X-ray diffraction study were obtained at 4 °C from its solution in pyridine. They were stable to air and moisture, moderately light-sensitive, and slightly soluble in common organic solvents.

The displacement of the carbene by pyridine is a novel reaction for silver N-heterocyclic carbene complexes and must arise from the relatively weak silver(I)−carbene bond in **2**, as suggested by the X-ray data. In comparison to polymer **2**, polymer **3** possesses a much tighter (Ag−I)$_n$ main framework, as shown by the shorter bond

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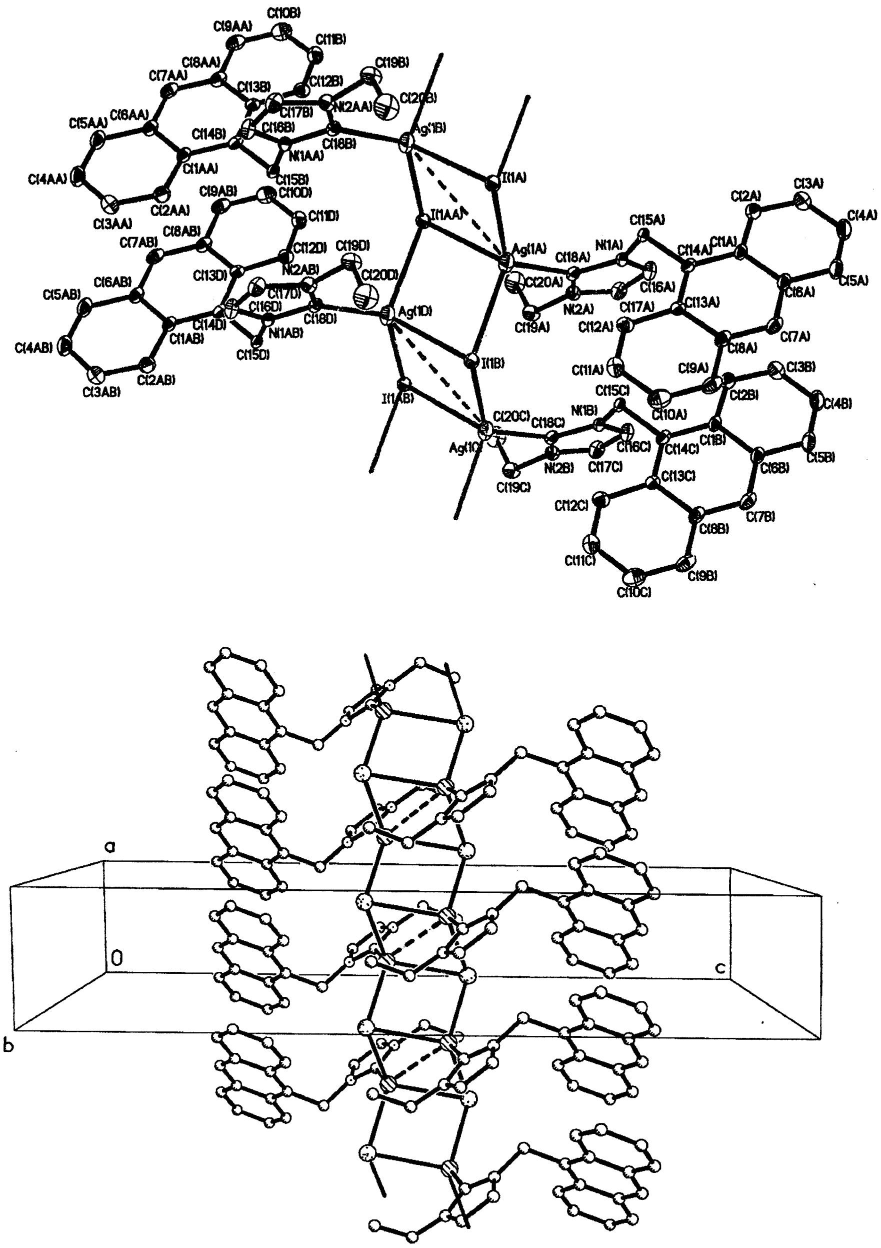

Figure 2. (a, top) Perspective view of **2** and anisotropic displacement parameters depicting 30% probability. Hydrogen atoms have been omitted for clarity. (b, bottom) Polymeric chain structure of **2**.

lengths: e.g., the Ag–Ag distances of 2.966 and 3.162 Å (Table 1). The dihedral angle of the rectangular planes remained the same as those of **2**. Thus, a probable argentophilic interaction was revealed by the absorption peak at 276 nm (see Figure 5a), which could be assigned to a spin-allowed $^1(d_{\sigma*} \rightarrow p_\sigma)$ transition.[12] The absorption at 256 nm most likely was due to the intraligand transition of pyridine.[13] Polymer **3** gave emission bands at 292 and 579 nm (trace 2 in Figure 5b); the former was clearly fluorescence derived from a pyridine singlet excited state, as demonstrated by the nicely symmetrical excitation spectrum at about 270 nm (trace 1 in Figure 5b). The latter broad 579 nm peak was also shown to originate from the excitation of the 270 nm region and must arise from the Ag–Ag interaction. This band was assigned as phosphorescence derived from the triplet excited state $(d_{\sigma*})^1(p_\sigma)^1$, in analogy to previous analysis.[14]

Further investigation of the photophysical behavior of polymer **2** and the synthesis of new luminescent organometallic polymers from precurcor **1** are being carried out, and it is expected that this type of polymer could possess some novel properties of optoelectronic materials.[15]

Experimental Section

General Comments. All manipulations were performed using Schlenk techniques. All the reagents for syntheses and analyses were of analytical grade and used without further purification. Melting points were determined with a Boetius Block apparatus. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded

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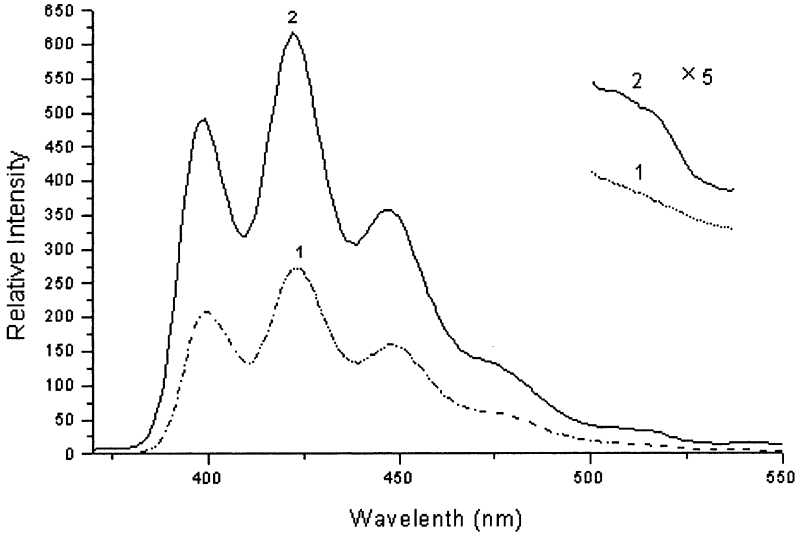

Figure 3. Emission spectra of precursor **1** (· – ·) and polymer **2** (—) at 298 K upon excitation at 256 nm in CH_2Cl_2 (5.0×10^{-6} M).

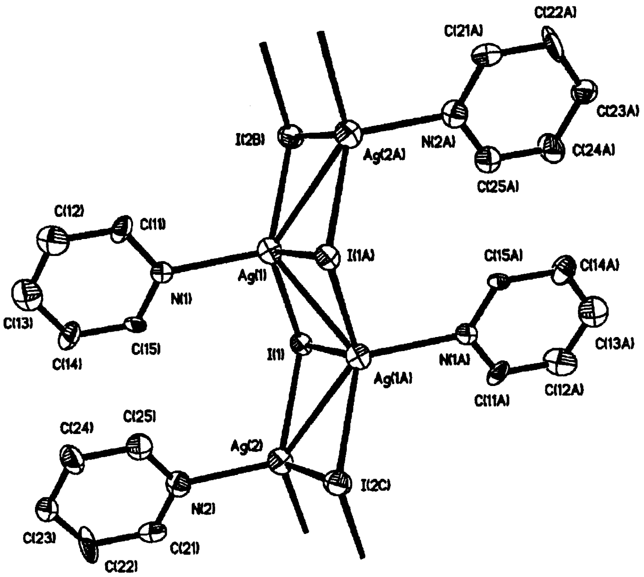

Figure 4. Perspective view of **3** and anisotropic displacement parameters depicting 30% probability. Hydrogen atoms have been omitted for clarity.

on a Varian Mercury Vx 300 spectrometer at 300 and 75 MHz, respectively. Chemical shifts, δ, are reported in ppm relative to the internal standard TMS for both ^1H and ^{13}C NMR. Mass spectra were recorded on a VG ZAB-HS spectrometer. Elemental analyses were obtained using a Perkin-Elmer 2400C elemental analyzer. The luminescent intensities of **1**–**3** were measured using a Cary Eclipse fluorescence spectrophotometer.

1-(9-Anthracenylmethyl)-3-ethylimidazolium Iodide (1). A 1,4-dioxane solution of imidazole (0.601 g, 8.83 mmol) was added to a suspension of oil-free sodium hydride (0.233 g, 9.71 mmol) in 1,4-dioxane (100 mL), and the mixture was stirred for 1 h at 90 °C. Then a 1,4-dioxane (50 mL) solution of 9-(chloromethyl)anthracene (2.000 g, 8.83 mmol) was added dropwise to the above solution. The mixture was stirred for 22 h at 90 °C; a brown solution was obtained. The solvent was removed with a rotary evaporator, and H_2O (300 mL) was added to the residue. Then the solution was extracted with CH_2Cl_2 (3×50 mL); the extracting solution was dried with anhydrous $MgSO_4$ and boiled with decolorizing charcoal. After CH_2Cl_2 was removed, a yellow solid was obtained, which was recrystallized from CH_2Cl_2/ether to give a yellow powder of 1-(9-anthracenylmethyl)imidazole. Yield: 2.132 g (94%). Mp: 154–156 °C. Anal. Calcd for $C_{18}H_{14}N_2$: C, 83.69; H, 5.46; N, 10.84. Found: C, 83.37; H, 5.74; N, 10.48. ^1H NMR (300 MHz, DMSO-d_6): δ 6.26 (s, 2H, CH_2An) (An = anthracene), 6.79 and 6.94 (s, 2 × 1H, 4,5-imi*H*) (imi: imidazole), 7.60 (t, *J* = 8.2 Hz, 2H, An*H*), 7.67 (t, *J* = 8.2 Hz, 2H, An*H*), 7.76 (s, 1H, An*H*), 8.16 (d, *J* = 8.2 Hz, 2H, An*H*), 8.55 (d, *J* = 8.2 Hz, 2H, An*H*), 8.71 (s, 1H, 2-imi*H*). ^{13}C NMR (75 MHz, DMSO-d_6): δ 43.5

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1–3

Compound **1**			
N(1)–C(18)	1.335(7)	N(2)–C(17)	1.334(8)
N(1)–C(16)	1.379(7)	C(16)–C(17)	1.331(9)
N(2)–C(18)	1.331(8)		
C(16)–N(1)–C(18)	106.5(5)	C(17)–C(16)–N(1)	107.8(6)
C(18)–N(2)–C(17)	108.7(6)	N(1)–C(18)–N(2)	108.8(6)
C(16)–C(17)–N(2)	108.1(6)		
Compound **2**			
Ag(1A)–C(18A)	2.182(7)	N(1A)–C(16A)	1.369(9)
Ag(1A)–I(1AA)	2.872(13)	C(18A)–N(2A)	1.348(9)
Ag(1A)–I(1A)	2.921(13)	N(2A)–C(17A)	1.371(10)
Ag(1A)–I(1B)	3.010(15)	C(16A)–C(17A)	1.346(11)
N(1A)–C(18A)	1.361(9)		
C(18A)–Ag(1A)–I(1AA)	125.9(18)		
C(18A)–Ag(1A)–I(1A)	111.7(18)		
C(18A)–Ag(1A)–I(1B)	111.8(18)		
I(1AA)–Ag(1A)–I(1B)	104.2 (4)		
I(1A)–Ag(1A)–I(1B)	108.4(3)		
I(1AA)–Ag(1A)–I(1A)	92.7(3)		
Ag(1A)–I(1AA)–Ag(1B)	87.3 (3)		
Ag(1A)–I(1B)–Ag(1D)	71.7(3)		
C(18A)–N(1A)–C(16A)	111.1(6)		
C(18A)–N(2A)–C(17A	111.5(6)		
C(16A)–C(17A)–N(2A)	106.6(6)		
C(17A)–C(16A)–N(1A	106.8(7)		
N(1A)–C(18A)–N(2A)	103.9(6)		
Compound **3**			
Ag(1)–N(1)	2.335(9)	Ag(1)–I(1A)	2.857(3)
Ag(1)–I(2B)	2.786(2)	Ag(1)–Ag(1A)	2.966(3)
Ag(1)–I(1)	2.840(3)	Ag(1)–Ag(2A)	3.162(2)
N(1)–Ag(1)–I(2B)	113.5(3)	I(1)–Ag(1)–I(1A)	117.3(6)
N(1)–Ag(1)–I(1)	101.3(3)	Ag(2)–I(1)–Ag(1)	108.6(8)
I(2B)–Ag(1)–I(1)	108.9 (8)	Ag(2)–I(1)–Ag(1A)	68.1(7)
(1)–Ag(1)–I(1A)	103.8(4)	Ag(1)–I(1)–Ag(1A)	62.7(6)
I(2B)–Ag(1)–I(1A)	111.7(8)		

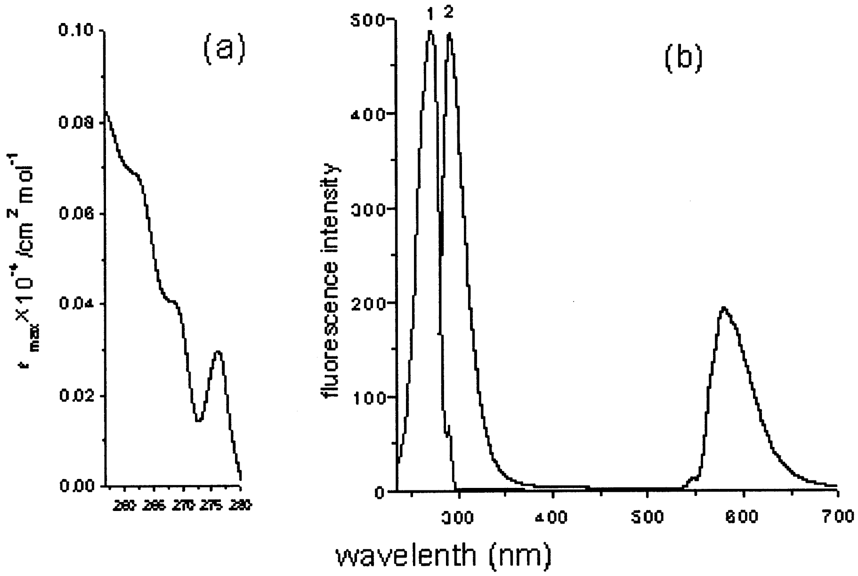

Figure 5. (a) UV−vis absorption spectrum (in CH_2Cl_2) and (b) excitation (1) and emission (2) spectra (room temperature; excitation at 272 nm) of polymer **3**.

(N*C*H_2An), 119.2 (4- or 5-imi*C*), 122.6, 122.8, 123.2, and 124.0 (An*C* or 4- or 5-imi*C*), 125.1, 125.4, 127.2, 127.6, 129.5, 129.7, 130.8, 131.4, and 134.1 (An*C*), 136.2 (2-imi*C*),

A solution of 1-(9-anthracenylmethyl)imidazole (2.000 g, 7.75 mmol) and ethyl iodide (2.417 g, 15.50 mmol) in 1,4-dioxane (50 mL) was stirred for 2 days at 60 °C. A yellow precipitate was formed, which was filtered and washed with acetone. Recrystallization from CH_2Cl_2/acetone give a yellow powder, 1-(9-anthracenylmethyl)-3-ethylimidazolium iodide (**1**). Yield: 2.968 g (93%). Mp: 196−198 °C. Anal. Calcd for $C_{20}H_{19}IN_2$: C, 57.98; H, 4.62; N, 6.76. Found: C, 57.63; H, 4.74; N, 6.33. ^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ 1.33 (t, $J = 7.5$ Hz, 3H, C*H*$_3$), 4.12 (q, $J = 7.5$ Hz, 2H, C*H*$_2$), 6.49 (s, 2H, C*H*$_2$An), 7.63 (t, $J = 8.4$ Hz, 2H, An*H*), 7.68 and 7.80 (s, 2 × 1H, 4, 5-imi*H*), 7.70 (t, $J = 8.4$ Hz, 2H, An*H*), 8.24 (d, $J = 8.4$ Hz, 2H, An*H*), 8.48 (d, $J = 8.4$ Hz, 2H, An*H*), 8.86 (s, 1H, An*H*), 9.00 (s, 1H, 2-imi*H*). ^{13}C NMR (75 MHz, DMSO-*d*$_6$): δ 15.7 (CH_2*C*H_3), 44.9 (N*C*H_2CH_3), 45.6 (N*C*H_2An), 122.8, 123.2, and 124.1 (An*C* or 4,5-imi*C*), 126.3, 128.4, 130.0, 130.8, 131.3, and 131.7 (An*C*), 136.0 (2-imi*C*).

1-(9-Anthrecenylmethyl)-3-ethylimidazol-2-ylidene Silver Iodide Polymer (2). Silver oxide (0.056 g, 0.24 mmol) was added to a solution of compound **1** (0.200 g, 0.48 mmol) in dichloromethane (30 mL), and the suspension was heated at reflux for 2 days at 40 °C. The suspension was filtered, and the filtrate was concentrated to 15 mL, on standing at 4 °C overnight, to afford polymer **2** as an air- and moisture-stable and moderately light-sensitive yellow crystalline solid. Yield: 0.126 g (50%). Mp: 180 °C dec. Anal. Calcd for $C_{20.5}H_{20}AgClIN_2O_{0.5}$: C, 43.00; H, 3.52; N, 4.89. Found: C, 42.55; H, 3.17; N, 4.53. FAB/MS: *m*/*z* 520 [M]$^+$ (10%), 287 [M − AgI]$^+$ (8%). ^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ 1.16 (t, $J = 7.2$ Hz, 3H, C*H*$_3$), 3.75 (q, $J = 7.2$ Hz, 2H, C*H*$_2$), 6.13 (s, 2H, C*H*$_2$An), 7.23 and 7.37 (s, 2 × 1H, 4,5-imi*H*), 7.54 (m, 4H, An*H*), 8.12 (d, $J = 8.2$ Hz, 2H, An*H*), 8.34 (d, $J = 8.2$ Hz, 2H, An*H*), 8.73 (s, 1H, An*H*). ^{13}C NMR (75 MHz, DMSO-*d*$_6$): δ 17.2 (CH_2*C*H_3). 46.9 and 47.0 (N*C*H_2CH_3 and N*C*H_2An), 121.5, 122.5, and 124.4, (An*C* or 4,5-imi*C*), 126.0, 126.9, 127.9, 128.4, 129.9, 131.0, and 131.8 (An*C*), 179.5 ($C_{carbene}$).

Pyridine Silver Iodide Polymer (3). A suspension of polymer **2** (0.100 g, 0.18 mmol) in pyridine (20 mL) was heated at reflux for 24 h to give a yellow solution. The latter was filtered and concentrated to 5 mL. On standing at 4 °C overnight it gave polymer **3** as a moderately light-sensitive, colorless, crystalline solid. Yield: 0.053 g (87%). Mp: >360 °C. Anal. Calcd for C_5H_5AgIN: C, 19.13; H, 1.60; N, 4.46. Found: C, 19.00; H, 1.83; N, 4.37. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99 (br, 2H, py*H*), 8.51 (br, 1H, py*H*), 8.89 (br, 2H, py*H*).

Table 2. Summary of Crystallographic Data for 1−3

	1	2	3
chem formula	$C_{20.50}H_{20}ClIN_2$	$C_{20.}H_{20}AgCl$-$IN_2O_{0.5}$	C_5H_5AgIN
fw	456.73	572.61	313.87
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a/Å	11.497(17)	4.572(2)	9.164(7)
b/Å	12.005(18)	18.450(9)	16.819(12)
c/Å	15.87(2)	25.441(12)	9.389(7)
α/deg	70.61(3)	90	90
β/deg	78.22(3)	91.154(8)	106.311(12)
γ/deg	81.35(3)	90	90
V/Å^3	2014(5)	2145.7(17)	1388.8(17)
Z	4	4	4
D_{calcd}, Mg/m^3	1.506	1.773	3.002
abs coeff, mm^{-1}	1.727	2.511	7.241
F(000)	908	1112	1136
cryst size, mm	0.35 × 0.30 × 0.25	0.20 × 0.20 × 0.15	0.30 × 0.25 × 0.20
θ_{min}, θ_{max}, deg	1.81, 25.03	2.35, 25.02	2.32, 25.02
T/K	293(2)	293(2)	293(2)
no. of data collected	8282	8665	5486
no. of unique data	6991	3755	2380
no. of refined params	442	248	184
goodness of fit on F^2 [a]	0.944	1.018	1.022
final R indices[b] ($I > 2\sigma(I)$)			
R1	0.0475	0.0483	0.0603
wR2	0.0960	0.1141	0.1504
R indices (all data)			
R1	0.1093	0.0721	0.0893
wR2	0.1157	0.1257	0.1817

[a] GOF = $[\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of parameters refined. [b] R1 = $\sum(||F_o| - |F_c||)/\sum|F_o|$; wR2 = $1/[\sigma^2(F_o^2) + (0.0691P) + 1.4100P]$, where $P = (F_o^2 + 2F_c^2)/3$.

X-ray Crystallography. For each of the compounds **1**−**3**, a selected single crystal was mounted on a Bruker SMART 1000 CCD diffractometer operating at 50 kV and 20 mA using Mo Kα radiation (0.710 73 Å). Data collection and reduction were performed using the SMART and SAINT software,[16] with frames of 0.6° oscillation in the θ range $1.8 < \theta < 25°$. An empirical absorption correction was applied using the SADABS program.[17] The structures were solved by direct methods, and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using the SHELXTL package.[18] All hydrogen atoms were generated geometrically (C−H bond lengths fixed at 0.96 Å), assigned appropriated isotropic thermal parameters, and included in structure factor calculations. The selected bond lengths and angles for **1**−**3** were given in Table 1. Crystal structure data and refinement details are summarized in Table 2.

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Supporting Information Available: Crystallographic data in CIF format for **1**−**3** and figures giving NMR spectra for the compounds prepared in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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