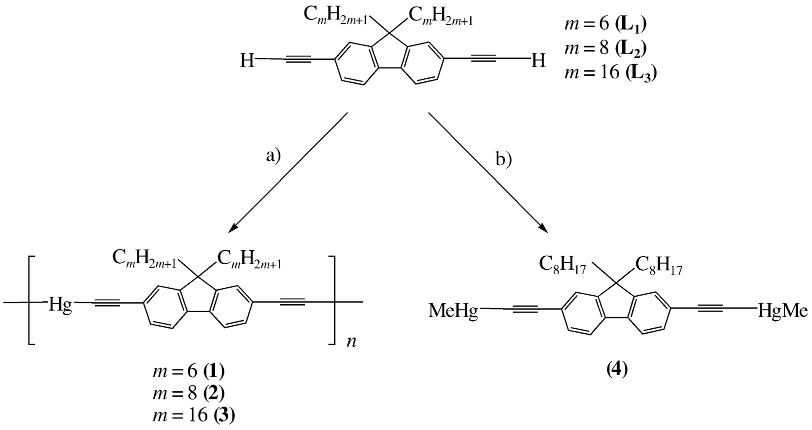
Emission in Hg^{II} Polymers

Triplet Emission in Soluble Mercury(II) Polyyne Polymers[**]

Wai-Yeung Wong,[*] Li Liu, and Jian-Xin Shi

Dedicated to Professor The Lord Lewis
on the occasion of his 75th birthday

Following the report of the first soluble metal polyyne oligomers by Hagihara et al.[1a], there is growing interest in the chemical and photophysical properties of conjugated polymetallaynes of group 8, 9, and 10 transition metals. These metal-based polymers provide model systems to explain the electronic properties of conjugated organic polymers used in light-emitting diodes.[1] In the past two decades, much has been discovered about the photoluminescent behavior of oligomeric and polymeric acetylides of platinum(II) and gold(I) complexes, where spin-forbidden triplet emissions (phosphorescence) can be identified clearly.[2,3] However, there is relatively little understood about the d^{10} mercury(II) system. To our knowledge, there are no literature reports on the photophysics and structural properties of soluble mercury-based polyynes. Although linear polymeric copper and mercury acetylides of the form $[\text{-M-C}\equiv\text{C-}p\text{-C}_6\text{H}_4\text{-C}\equiv\text{C-}]_n$ were reported as early as 1960, these materials were often found to be insoluble and intractable, which hampered their purification and characterization.[1a] The group 12 heavy mercury atom, with its propensity to enhance spin–orbit coupling, could be an ideal candidate for harvesting the energy of triplet excitons.[1b,4] We report here the first examples of soluble well-defined high-molecular-weight mercury(II) polyyne polymers with 9,9-dialkylfluorene groups, from which we have been able to directly trigger $^3(\pi\pi^*)$ emissions localized on the organic system through efficient intersystem crossing (ISC) by ligation to the Hg^{II} moiety.



Scheme 1. Synthesis of **1–4**: a) $HgCl_2$, NaOH, MeOH; b) MeHgCl, NaOH, MeOH.

The synthesis of the new polymers **1–3** is shown in Scheme 1. Mercuration of 9,9-dialkyl-2,7-diethynylfluorenes **L$_1$–L$_3$** with $HgCl_2$ using methanolic NaOH at room temperature produced a pale-yellow suspension and the solids were collected by filtration to afford off-white air-stable products **1–3** in high yields and purity. Their excellent film-forming properties suggest a macromolecular nature for the materials, and their good solubilities in CH_2Cl_2 and $CHCl_3$ render them amenable to spectroscopic studies and readily solution-processable for optical characterization. Estimates of the molecular weights using GPC in THF indicate a high degree of polymerization (DP = 24–47) in these polyynes (Table 1) and the absence of end-group NMR resonances is evidence of their high molecular weight. A similar synthetic route using 2,7-diethynylfluorene ($m = 0$ in Scheme 1) only afforded an intractable solid and thus the use of long alkyl chains is crucial in achieving highly soluble polymers. Complex **4**, as a model complex of polymer **2**, was also synthesized by treatment of **L$_2$** with two equivalents of MeHgCl, in which one coordination site is protected by a Me group, under similar basic conditions.[5] The symmetrical nature of the molecules was ascertained by NMR studies. Notably, two distinct ^{13}C NMR signals for the sp carbon atoms of the acetylenic units were observed for **1–4**, and they are shifted downfield with respect to the free alkynes, consistent with the formation of Hg–C(sp) bond. Only six peaks appeared in the aromatic region of their ^{13}C NMR spectra, which relate to the 12 aromatic carbon atoms in the structures of **1–4**; these data indicate high structural regularity in the polymers. Complex **4** displayed a single ^{199}Hg NMR peak at $\delta = -453$ (compared with $\delta = -847$ for MeHgCl), which reflects the polarization of the Hg–C≡ bonds.[6] The molecular structure of **4**, as confirmed by X-ray crystallography,[7] also helped to establish polymer structures in the solid state and to correlate the photophysical properties with the structural data. The structure of **4** consists of dinuclear molecules in which the mercury centers adopt a two-coordinate linear geometry in a rigid-rod manner (Figure 1). The lattice structure is highlighted by the presence of weak intermolecular noncovalent Hg⋯Hg interactions (3.738 and 4.183 Å), which link the molecular units together to form a loose polymeric structure in a 3D network (Figure 2).[5b,c] The Hg⋯Hg separations in **4** are comparable to the values of 3.71–4.25 Å for $[Hg(C\equiv CR)_2]$ (R = Ph, $SiMe_3$) and are toward the upper limit of those accepted as representing metallophilic interactions.[8]

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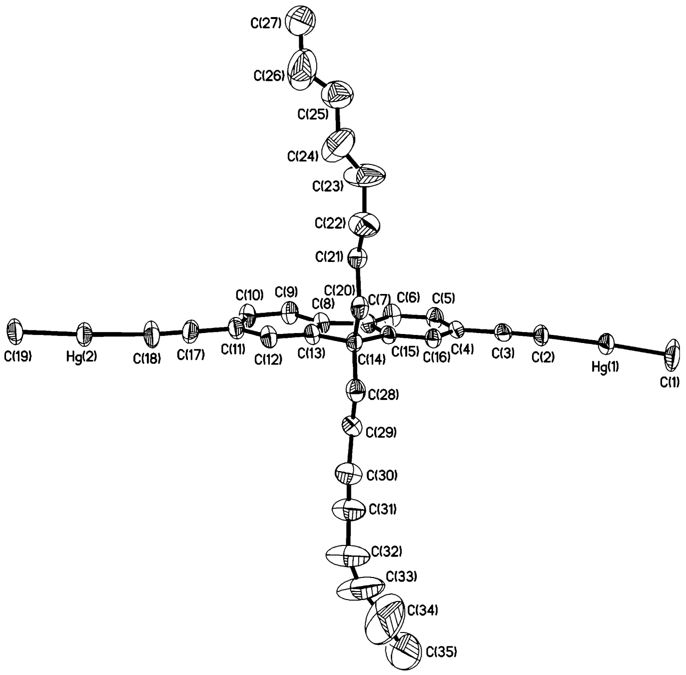

Figure 1. Molecular structure of the model complex **4**, with thermal ellipsoids shown at the 25 % probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Hg(1)-C(1) 2.080(11), Hg(1)-C(2) 2.045(8), Hg(2)-C(18) 2.044(9), Hg(2)-C(19) 2.059(9), C(2)-C(3) 1.186(11), C(17)-C(18) 1.209(13); C(1)-Hg(1)-C(2) 177.6(7), Hg(1)-C(2)-C(3) 176.8(8), C(18)-Hg(2)-C(19) 177.7(5), Hg(2)-C(18)-C(17) 176.1(12).

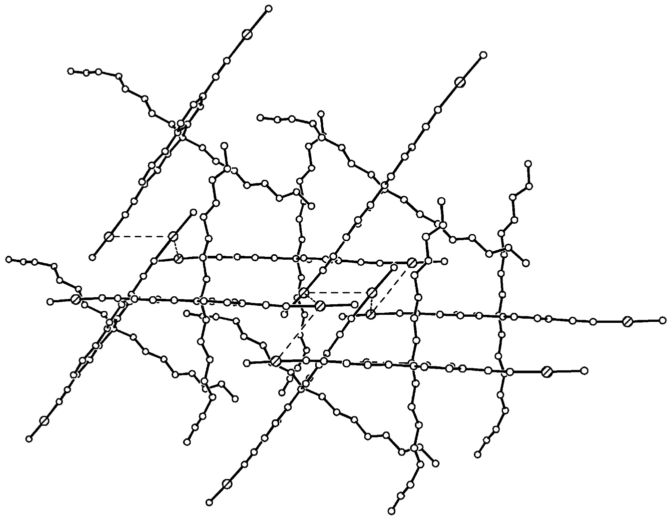

Figure 2. Crystal packing diagram for **4** showing the weak intermolecular Hg⋯Hg contacts in a 3D network.

Table 1: Structural and thermal properties of **1**–**3**.

polymer	M_w[a]	M_n[a]	M_w/M_n	DP	T_{decomp} [°C][b]
1	28720	27100	1.06	47	282 ± 5
2	18320	15090	1.22	24	220 ± 5
3	38650	36250	1.07	42	200 ± 5

[a] Calibration against polystyrene. [b] Onset temperature.

The thermal properties of the polymers were examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC; heating rate 20 °C min^{-1}). Polymers **1**–**3** displayed moderate thermal stability with decomposition temperatures greater than 200 °C (Table 1), and exhibited an exotherm coincident with the mass lost due to decomposition. Polymer **3** showed the lowest onset decomposition temperature, while **1** and **2** with shorter alkyl chains exhibited increasing decomposition temperatures with decreasing *m* value. Each showed two stepwise losses in the thermogravimetric curve, which correspond to the elimination of two alkyl groups from their respective molecules.

The photophysical data of **1**–**4** are shown in Table 2. They all display similarly structured absorption bands in the near-UV region. These bands are mainly associated with the organic $^1(\pi\pi^*)$ transitions, possibly with some admixture of metal orbitals, and the 0–0 absorption peak is assigned as the $S_0 \rightarrow S_1$ transition.[5b,9] As compared with **L$_1$**–**L$_3$**, we noted a red-shift in the absorption and emission bands of **1**–**4** after the inclusion of a heavy metal atom, which indicates an increase in π-conjugation. The C-9 substituents on the fluorene ring exert a minimal effect on the absorption energies, and comparable optical band gaps (E_{gap}) are noted for **1**–**3** (Figure 3 a). The transition energies of polymer **2** are lowered with respect to those of the monomer **4**, which suggests that a well-extended singlet excited state exists in the polymers.[1c,9b,9d] Bathochromic shifts of about 10 nm are observed for the lowest-energy absorption bands of **1**–**4** in the solid state. Examination of the absorption behavior of the polymers in $CHCl_3$, $CHCl_3$/MeOH solutions, and in the solid state, corroborates the presence of solid-state aggregates in thin films.[10] For instance, the addition of a nonsolvent (MeOH) to a $CHCl_3$ solution of **2** leads to the development of a new band centered at 365 nm, which corresponds to the strongest absorption observed in the solid state (Figure 4). Further support for the red shift is provided by the observation of solid-state mercuriophilic interactions in the crystal structure of the model compound **4** (see above).[5b,8]

Table 2: Photophysical data for **1**–**4**.

	λ_{max} [nm] CH$_2$Cl$_2$	λ_{max} [nm] film	E_{gap} [eV]	λ_{em} [nm] CH$_2$Cl$_2$ (290 K)[b]	film (290 K)	film (11 K)
1	313, 341, 355	316, 345, 365	3.32	381, 406* (0.003)[c]	475br	427, 570, 610*
2	313, 340, 355	316, 345, 364	3.31	382, 406* (0.004)[c]	477br	426, 583, 630*
3	313, 338, 355	316, 345, 364	3.32	385*, 409 (0.007)[c]	478br	429, 590, 634*
4	311 (4.7), 330 (4.9), 346 (5.0)[a]	316, 339, 358	3.38	374 (0.02)[d]	417, 435, 477br	416, 438, 544*, 591*

[a] logε. [b] Fluorescence quantum yields in parentheses are measured relative to quinine sulfate in 0.1 N H_2SO_4 ($\Phi = 0.54$). [c] $\lambda_{ex} = 328$ nm. [d] $\lambda_{ex} = 340$ nm. Asterisks indicate that emission peaks appear as shoulders or weak bands. br = broad.

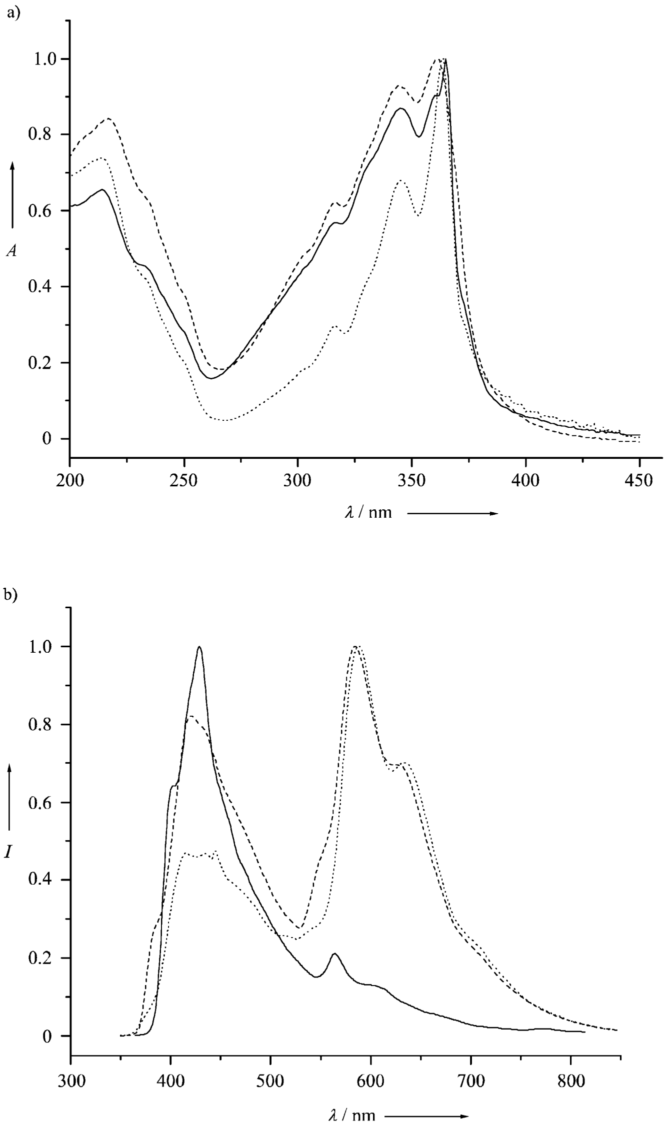

Figure 3. a) Absorption and b) emission spectra (11 K) of thin solid films of **1** (——), **2** (-----) and **3** (•••••).

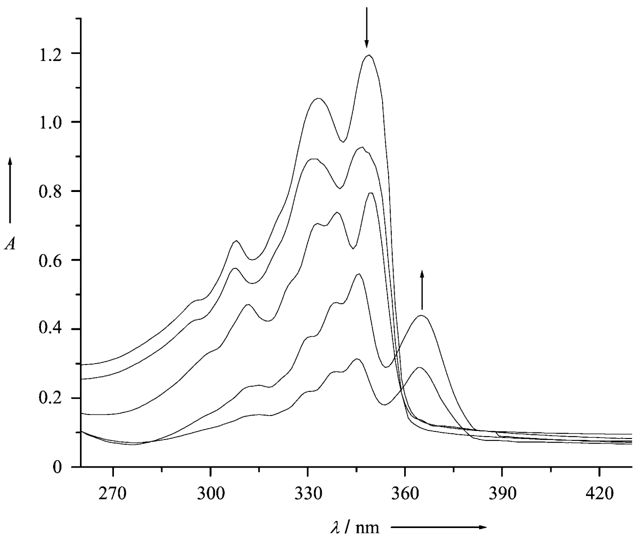

Figure 4. Absorption spectrum of **2** ($CHCl_3$) upon the addition of MeOH (top to bottom: 0, 20, 40, 80, 90%).

The long side chains in polymers **1**–**3** should suppress aggregation or at least delay its onset, and indeed, changes in absorptions are observed for **2** after the addition of approximately 80% methanol. The behavior of **1**–**3** is analogous to that of the poly[(9,9-dialkyl)fluoren-2,7-yleneethynylene]s, 2,5-dialkylpoly(*p*-phenylene-ethynylenes), and polydiacetylenes, where similar aggregate bands are described.[10]

The photoluminescence (PL) spectra display a red shift on going from binuclear to polynuclear structures (e.g., **2** versus **4**), which implies that the excited state is stabilized by the greater degree of delocalization in the polymers. However, we cannot rule out the possibility that the shifts are related to the number and/or strength of the Hg···Hg interactions in the polymers. In dilute fluid solutions, we observe an intense $^1(\pi\pi^*)$ emission peak near 400 nm for **1**–**4** due to fluorescence ($S_1 \rightarrow S_0$), which is in line with the small Stokes shift observed between the bands in the absorption and the emission spectra.[2,9] Comparing these results with the solution PL data, the thin-film singlet emissions in **1**–**4** appear broad at 290 K and are red-shifted, which is consistent with their absorption features, and is likely to be a result of interchain interactions due to aggregate formation.[11] At 11 K, another well-resolved lower-lying emission emerges at around 570–590 nm for polymers **1**–**3** and the large Stokes shifts of these peaks from the dipole-allowed absorptions (approximately 1.2–1.3 eV), plus the long emission lifetimes at 11 K (28 ± 0.2 (**1**), 35 ± 0.2 (**2**), and 42 ± 0.2 µs (**3**)) are indicative of their triplet parentage; thus, they are assigned to the $^3(\pi\pi^*)$ excited states of the diethynylfluorenes (Figure 3b).[9] The triplet emission ($T_1 \rightarrow S_0$) bands increase in intensity with decreasing temperature for **1**–**3** (see Supporting Information) and show vibronic structure at low temperatures, typical of the phosphorescence observed in related Pt^{II} and Au^{I} polyynes.[2,3,9] We found that the intensity of the phosphorescence relative to fluorescence increases as the value of *m* increases from **1** ($m = 6$) to **3** ($m = 16$); this phenomenon probably results from a reduced number of quenching sites through mono- or bimolecular decay processes in **3**, which has longer alkyl chains.[2a] To assess the relative ISC efficiency based on the peak height ratio from triplet emission to singlet emission at 11 K, we note that the order of S_1–T_1 crossover efficiency is **3** > **2** > **1** (Figure 3b). The ISC rate is also higher in the polymers than in the monomers (that is, **2** versus **4**). Considering the spatial extent of the singlet and triplet excitons in our systems, values of $\Delta E(S_0–T_1)$ (energy gap between S_0 and T_1) were found to be 2.10–2.23 eV for **1**–**3**, which can be compared to those observed in dialkoxy-substituted poly(*p*-phenyleneethynylene)s (PPEs, 1.90 eV),[12] [Cy_3PAu]-capped PPEs (1.98–2.04 eV),[3a] and Pt-containing poly[(9,9-dialkyl)fluoren-2,7-yleneethynylene]s (2.20 eV).[9a,b] The $\Delta E(S_1–T_1)$ values for **1**–**3** lie within the range of 0.73–0.79 eV, which corresponds well with the S_1–T_1 energy gap of 0.7 ± 0.1 eV for similar π-conjugated Pt and Au polyynes,[2,3a] and are close to the gaps estimated for a series of related organic polymers.[13] We attribute such a constant $\Delta E(S_1–T_1)$ value to the exchange energy and possibly some additional constant contribution which results from the admixture of the Hg orbitals.[2b] Similar to the Pt polyynes, the use of mercury in **1**–**3** together with their associated large optical band gaps can offer a good route towards the enhancement of the ISC rate, and we have shown for the first time that the organic triplet emissions of fluorenyleneethynylenes have been "illuminated" by the heavy-atom effect of mercury. The present investigation is desirable for applications that harvest the T_1 state for light emission and will provide impetus for future study.

Experimental Section

1–**3**: A solution of $HgCl_2$ (0.60 g, 2.21 mmol) in MeOH (10 mL) was mixed with $\mathbf{L_2}$[9a,b] (0.97 g, 2.21 mmol) in MeOH (10 mL). To this mixture, 28 mL of basic MeOH (5.60 mmol; prepared by dissolving 0.40 g of NaOH in 50 mL of MeOH) was added. Within a few minutes, a light-yellow solid precipitated from the homogeneous solution. The solid was then collected by filtration after stirring for 12 h, washed with MeOH (2 × 20 mL), and air-dried to furnish **2** in 87% yield (1.23 g). IR (KBr): $\tilde{\nu} = 2140\ \text{cm}^{-1}$ ($C\equiv C$); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, TMS): $\delta = 7.58$–7.55 (m, 2H; Ar), 7.43–7.40 (m, 4H; Ar), 1.87 (m, 4H; $CH_2(CH_2)_5$), 1.18–0.86 (m, 20H; $(CH_2)_5$), 0.76 (t, 6H; CH_3, $^3J(H,H) = 7.2$ Hz), 0.51 ppm (m, 4H; CH_2CH_3); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K, TMS): $\delta =$ 151.03, 140.83, 131.43, 126.65, 120.80 (Ar), 119.98 (Ar), 106.83 ($C\equiv C$), 84.51 ($C\equiv C$), 55.27 (quat C), 40.35, 31.85, 30.07, 29.32, 23.82, 22.68, and 14.21 ppm (C_8H_{17}); elemental analysis calcd (%) for $(C_{33}H_{40}Hg)_n$: C 62.20, H 6.33; found: C 61.98, H 6.20. Polymers **1** and **3** were prepared similarly from $\mathbf{L_1}$ and $\mathbf{L_3}$; they were both isolated as off-white solids in 93 and 82% yields, respectively. **1**: IR (KBr): $\tilde{\nu} = 2135\ \text{cm}^{-1}$ ($C\equiv C$); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, TMS): $\delta =$ 7.65–7.62 (m, 2H; Ar), 7.50–7.47 (m, 4H; Ar), 1.94 (m, 4H; $CH_2(CH_2)_3$), 1.11–0.91 (m, 12H; $(CH_2)_3$), 0.78 (t, 6H; CH_3, $^3J(H,H) = 7.3$ Hz), 0.57 ppm (m, 4H; CH_2CH_3); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K, TMS): $\delta = 150.92$, 140.74, 131.43, 126.61, 120.85 (Ar), 119.90 (Ar), 107.04 ($C\equiv C$), 84.52 ($C\equiv C$), 55.20 (quat C), 40.30, 31.57, 29.70, 23.75, 22.67, and 14.09 ppm (C_6H_{13}); elemental analysis calcd (%) for $(C_{29}H_{32}Hg)_n$: C 59.93, H 5.55; found: C 59.77, H 5.29. **3**: IR (KBr): $\tilde{\nu} = 2140\ \text{cm}^{-1}$ ($C\equiv C$); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, TMS): $\delta = 7.64$–7.61 (m, 2H; Ar), 7.49–7.46 (m, 4H; Ar), 1.96 (m, 4H; $CH_2(CH_2)_{13}$), 1.25–1.04 (m, 52H; $(CH_2)_{13}$), 0.87 (t, 6H; CH_3, $^3J(H,H) = 7.2$ Hz), 0.58 ppm (m, 4H; CH_2CH_3); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K, TMS): $\delta = 151.02$, 140.84, 131.43, 126.64, 120.75 (Ar), 119.96 (Ar), 106.83 ($C\equiv C$), 84.51 ($C\equiv C$), 55.33 (quat C), 40.36, 32.00, 30.11, 29.78, 29.76, 29.69, 29.44, 29.41, 29.36, 23.82, 22.79, and 14.24 ppm ($C_{16}H_{33}$); elemental analysis calcd (%) for $(C_{49}H_{72}Hg)_n$: C 68.30, H 8.42; found: C 68.05, H 8.21.

4: The diyne $\mathbf{L_2}$ (0.44 g, 1.00 mmol) in MeOH (10 mL) was first combined with MeHgCl (0.50 g, 2.00 mmol) in MeOH (10 mL). 0.20 M basic MeOH (13 mL) was subsequently added to give a pale-yellow suspension. The solvents were then decanted and the light-yellow solid **4** (0.69 g, 80%) was washed with MeOH (2 × 20 mL) and air-dried. IR (KBr): $\tilde{\nu} = 2120\ \text{cm}^{-1}$ ($C\equiv C$); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, TMS): $\delta = 7.58$–7.55 (m, 2H; Ar), 7.43–7.29 (m, 4H; Ar), 1.86 (m, 4H; $CH_2(CH_2)_5$), 1.21–0.82 (m, 20H; $(CH_2)_5$), 0.80 (t, 6H; CH_2CH_3, $^3J(H,H) = 8.0$ Hz), 0.68 (s, 6H; CH_3), 0.54 ppm (m, 4H; CH_2CH_3); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K, TMS): $\delta =$ 151.00, 140.49, 131.13, 126.49, 121.58 (Ar), 119.82 (Ar), 106.42 ($C\equiv C$), 84.48 ($C\equiv C$), 55.06 (quat C), 40.35, 31.75, 30.02, 29.26, 23.68, 22.56, and 14.08 ppm (C_8H_{17}); ^{199}Hg (48.2 MHz, $CDCl_3$, 298 K, Me_2Hg): $\delta = -453$ ppm; positive FAB-MS: m/z 868 $[M]^+$; elemental analysis calcd (%) for $C_{35}H_{46}Hg_2$: C 48.44, H 5.34; found: C 48.28, H 5.23.

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[7] Crystal data for **4**: $C_{35}H_{46}Hg_2$, $M_w = 867.90$, crystal dimensions $0.32 \times 0.19 \times 0.17\ \text{mm}^3$, monoclinic, space group Cc, $a = 21.8830(13)$, $b = 17.6803(13)$, $c = 9.2053(6)$ Å, $\beta = 107.840(2)°$, $V = 3390.3(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.700\ \text{g cm}^{-3}$, $\mu(Mo_{K\alpha}) = 9.065\ \text{mm}^{-1}$, $F(000) = 1664$, $T = 293$ K, $2\theta_{max} = 56.6°$. 10015 reflections measured, of which 5992 were unique ($R_{int} = 0.0419$). Final $R_1 = 0.0317$ and $wR_2 = 0.0702$ for 4357 observed reflections with $I > 2\sigma(I)$. CCDC-208083 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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