Supramolecular Stabilization of α,ω-Diphenylpolyynes by Complexation to the Tridentate Lewis Acid [o-C$_6$F$_4$Hg]$_3$

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The interaction of trimeric (perfluoro-*o*-phenylene)mercury ([*o*-C$_6$F$_4$Hg]$_3$, **1**) with α,ω-diphenylpolyynes containing 4, 6, 8, and 12 sp carbon atoms in CH$_2$Cl$_2$ leads to the formation of (**1**)$_2$·Ph(C≡C)$_2$Ph (**2**), **1**·Ph(C≡C)$_3$Ph (**3**), (**1**)$_2$·Ph(C≡C)$_4$Ph (**4**), and (**1**)$_2$·Ph(C≡C)$_6$Ph·CH$_2$Cl$_2$ (**5**). Adducts **2**−**4** have been characterized by elemental analysis, X-ray crystallography, infrared and fluorescence spectroscopy, differential scanning calorimetry, and thermogravimetric analysis. In the solid state, the α,ω-diphenylpolyynes, which are approximately planar, are associated to molecules of **1** on either side of the molecular plane via secondary Hg−π interactions. The acetylenic stretches of **2**−**5** measured by IR spectroscopy are essentially identical with those of the free polyyne. While adducts **3**−**5** give rise to only faint emissions upon UV irradiation, the luminescence spectrum of **2** indicates complete quenching of the fluorescence and displays a heavy-atom-induced emission whose energy and vibronic progression are identical with those reported for the phosphorescence of the pure diyne. DSC/TGA studies indicate that adducts **2**−**4** are more thermally stable than the respective free α,ω-diphenylpolyynes. For Ph(C≡C)$_4$Ph, the stability range is increased by almost 120 °C under an oxidizing atmosphere. Similar conclusions are derived by monitoring the acetylenic stretches of Ph(C≡C)$_4$Ph and **4** as a function of temperature in KBr.

Introduction

Carbyne, defined as an infinite chain of sp-hybridized carbon atoms, is a much discussed one-dimensional allotrope of carbon whose instability has complicated isolation and definitive characterization.[1] Similar complications are also encountered in the synthesis and isolation of short chains of sp-hybridized carbon atoms, namely polyynes. Literature reports indicates that derivatives such as Me$_3$C(C≡C)$_{12}$CMe$_3$ and Et$_3$Si(C≡C)$_8$SiEt$_3$ decompose within minutes at room temperature.[2,3] Similar observations are made with Ph(C≡C)$_4$Ph, which discolors within hours at room temperature.[4] Owing to these limitations, recent efforts have been directed to the development of methods allowing for the stabilization of polyynes.[5,6] For example, the use of (*i*-Pr)$_3$Si[7] moieties as end groups has led to the stabilization of C$_{20}$ polyynediyl chains. Remarkable results have also been obtained with *trans*-(*p*-tol)(*p*-tol$_3$P)$_2$Pt units which have been used to cap and stabilize C$_{28}$ polyynediyl chains.[8] Nonetheless, it remains that the exposed nature of the polyacetylenic chain is often associated with the instability of such derivatives, which tend to undergo photochemically[9,10] or thermally induced polymerization and oxidation reactions.[11] As a result, the incorporation of covalently bound end groups which can protect and thus insulate the more exposed part of the molecule has also been considered. Such an approach is nicely illustrated by the work of Gladysz, who reported a series of diplatinum polyynediyl complexes in which the polyyne is shielded by the alkanediyl chains of two bridging diphosphines.[12] Using a different approach, Hirsch was able to prepare a stable decayne bearing aromatic polyether dendrimers as end groups.[13]

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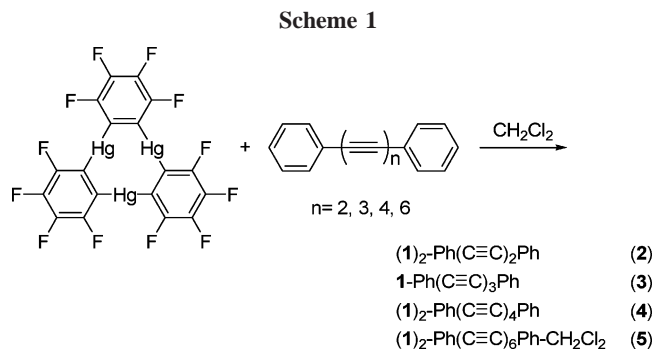**Table 1. Crystal Data and Data Collectionn and Structure Refinement Details for 2−5**

	2	3	4	5
		Crystal Data		
formula	$C_{52}H_{10}F_{24}Hg_6$	$C_{36}H_{10}F_{12}Hg_3$	$C_{28}H_5F_{12}Hg_3$	$C_{31}H_7Cl_2F_{12}Hg_3$
M_r	2294.14	1272.21	1171.09	1280.04
cryst size (mm³)	0.08 × 0.07 × 0.065	0.13 × 0.10 × 0.08	0.37 × 0.10 × 0.06	0.10 × 0.035 × 0.025
cryst syst	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P2_1/c$
a (Å)	9.0887(18)	12.360(3)	6.9766(14)	9.6848(19)
b (Å)	10.574(2)	30.321(6)	10.317(2)	7.1522(14)
c (Å)	13.650(3)	9.0688(18)	18.189(4)	43.542(9)
α (deg)	68.33(3)	90	95.01(3)	90
β (deg)	78.31(3)	108.43(3)	93.27(3)	95.49(3)
γ (deg)	83.00(3)	90	102.36(3)	90
V (Å³)	1192.2(4)	3224.4(11)	1270.1(4)	3002.3(10)
Z	1	4	2	4
ρ_{calcd} (g cm⁻³)	3.195	2.621	3.062	2.832
μ (mm⁻¹)	19.380	14.435	18.194	15.580
$F(000)$ (e)	1018	2296	1042	2300
		Data Collection		
T (K)	110(2)	110(2)	110(2)	110(2)
scan mode	ω	ω	ω	ω
hkl ranges	−10 → +10, −11 → +11, −15 → +15	−16 → +15, −39 → +39, −11 → +11	−7 → +7, −11 → +11, −20 → +20	−12 → +12, −8 → +9, −56 → +56
no. of measd rflns	6872	13 487	8031	23 337
no. of unique rflns [R_{int}]	3346 [0.0475]	3716 [0.0488]	3641 [0.0509]	6954 [0.0718]
no. of rflns used for refinement	3346	3716	3641	6954
		Refinement		
no. of refined params	370	231	388	433
R1,[a] wR2[b] ($I > 2\sigma(I)$)	0.0599, 0.1583	0.0336, 0.0853	0.0377, 0.0907	0.0528, 0.0956
ρ_{fin}(max, min) (e Å⁻³)	4.300, −4.879	2.056, −2.540	2.265, −1.968	1.750, −2.320

[a] R1 = $\Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] wR2 = $\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$; $P = (F_o^2 + 2F_c^2)/3$. For **2**, $a = 0.1166$ and $b = 0$; for **3**, $a = 0.0502$ and $b = 0$; for **4**, $a = 0.0377$ and $b = 5.9144$; for **5**, $a = 0.0252$ and $b = 26.1711$.

As shown by some of our recent work,[14−16] trimeric (perfluoro-*o*-phenylene)mercury[17,18] (**1**, [*o*-C_6F_4Hg]$_3$) "sticks" to the π face of aromatic substrates to form extended binary supramolecules in which both components alternate. In all cases, the mercury centers of the trinuclear mercury complex approach the π face of the substrate and engage in polyhapto secondary Hg−C interactions in the 3.3−3.6 Å range. Taking into account the affinity that mercury(II) cations display for alkynes,[19] we decided to determine if **1** could also form supramolecular adducts with polyynes. If successful, it occurred to us that such an approach may serve to enhance the stability of these otherwise highly reactive hydrocarbons.

Results and Discussion

Synthesis and Characterization of the Adducts 2−5. The formation of adducts involving **1** and α,ω-diphenylpolyynes with 4, 6, 8, and 12 sp carbon atoms was originally surveyed by mixing equimolar quantities of **1** with the corresponding α,ω-diphenylpolyynes in CH_2Cl_2 (Scheme 1). Slow evaporation of the solvent resulted in the crystallization of **1**·Ph(C≡C)₃Ph (**3**)

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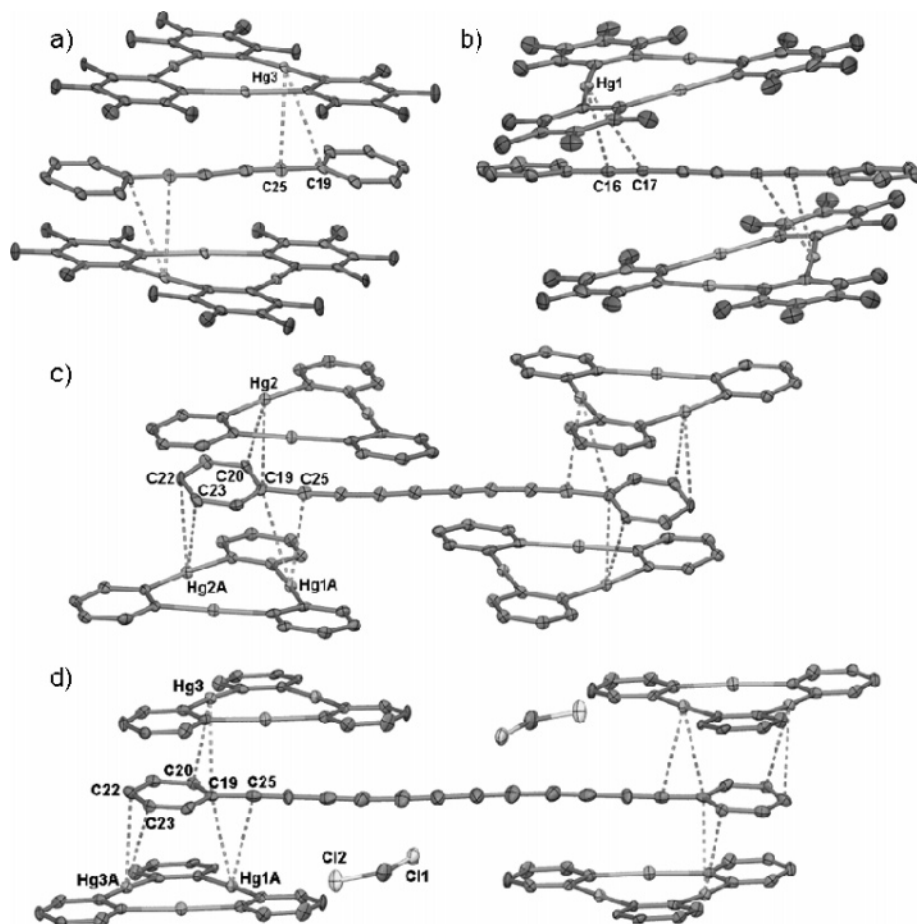(14) Haneline, M. R.; Taylor, R.; Gabbaï, F. P. *Chem. Eur. J.* **2003**, *9*, 5188−5193.

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Scheme 1

(1)₂-Ph(C≡C)₂Ph   (2)
1-Ph(C≡C)₃Ph   (3)
(1)₂-Ph(C≡C)₄Ph   (4)
(1)₂-Ph(C≡C)₆Ph-CH_2Cl_2 (5)

as a 1:1 adduct and (**1**)₂·Ph(C≡C)₂Ph (**2**) and (**1**)₂·Ph(C≡C)₄Ph (**4**) as 2:1 adducts. In all cases, varying the ratio of **1** to the α,ω-diphenylpolyynes in the starting mixtures did not affect the composition of the adducts. To optimize the yields of the 2:1 adducts, their syntheses were repeated by mixing 2 equiv of **1** with 1 equiv of the corresponding α,ω-diphenylpolyyne. Crystals of (**1**)₂·Ph(C≡C)₆Ph·CH_2Cl_2 (**5**) were obtained by chilling a 2:1 mixture of **1** and Ph(C≡C)₆Ph in CH_2Cl_2. The solution decomposition of the polyyne prior to crystallization is partly responsible for the low isolated yields of **3**−**5**, which do not exceed 40%. Adducts **2** and **3** are colorless, while adducts **4** and **5** display yellow hues which, a priori, correspond to the color of the pure polyynes. All adducts are air-stable. Crystals of **5**, however, quickly become opaque and brittle through partial loss of CH_2Cl_2 when removed from the mother liquor. These adducts can be dissolved in polar solvents such as acetone. ¹H and ¹⁹F NMR spectra of these adducts in d_6-acetone only show the resonances of the individual components, indicating complete dissociation.

The structures of **2**−**5** have been determined by X-ray crystallography (Table 1, Figure 1). In all cases, the α,ω-diphenylpolyynes, which are approximately planar, are associ-

Figure 1. Structures of (a) **2**, (b) **3**, (c) **4**, and (d) **5** (50% ellipsoids). Short intermolecular distances are represented by dotted lines. H atoms are omitted for **2**–**5**; F atoms are omitted for **4** and **5**. Selected intermolecular bond distances (Å): (a) Hg(3)−C(19) = 3.45, Hg-(3)−C(25) = 3.29; (b) Hg(1)−C(16) = 3.25, Hg(1)−C(17) = 3.42; (c) Hg(1)−C(27) = 3.34, Hg(2)−C(19) = 3.35, Hg(2)−C(20) = 3.42, Hg(1)−C(27) = 3.34, Hg(1A)−C(19) = 3.47, Hg(1A)−C(25) = 3.26, Hg(2A)−C(22) = 3.39, Hg(2A)−C(23) = 3.32; (d) Hg(1)−C(19) = 3.32, Hg(1)−C(25) = 3.36, Hg(3)−C(22) = 3.32, Hg(3)−C(23) = 3.40, Hg(3A)−C(19) = 3.35, Hg(3A)−C(20) = 3.18.

ated to molecules of **1** on either side of the molecular plane. As depicted in Figure 1, some of the phenyl and alkynyl carbon atoms of the polyynes are in contact with the mercury centers of **1**. The resulting Hg−C distances (3.18−3.47 Å) are within the sum of the van der Waals radii of mercury (1.7−2.0 Å)[20,21] and carbon (1.7 Å),[22] thus indicating the presence of secondary Hg−π interactions. Secondary Hg−π interactions of comparable length have been previously observed in arene adducts of **1**[14−16] and in the solid-state structures of various alkynylmercury derivatives.[23,24] These interactions are complemented, in the case of **2,** by an arene−fluoroarene interaction involving the phenyl rings of Ph(C≡C)$_2$Ph and a tetrafluorophenylene ring of **1**. While the solid-state structure of **2** consists of (**1**)$_2$·Ph(C≡C)$_2$Ph "sandwiches" piled on top of each other (Figure 2a), the supramolecular structure of **3** reveals the formation of extended stacks in which molecules of **1** and Ph(C≡C)$_3$Ph alternate regularly (Figure 2b). In **4** and **5**, which also adopt stacked structures, a molecule of the α,ω-diphenylpolyyne alternates with two molecules of **1** (Figure 2c,d). These two molecules of
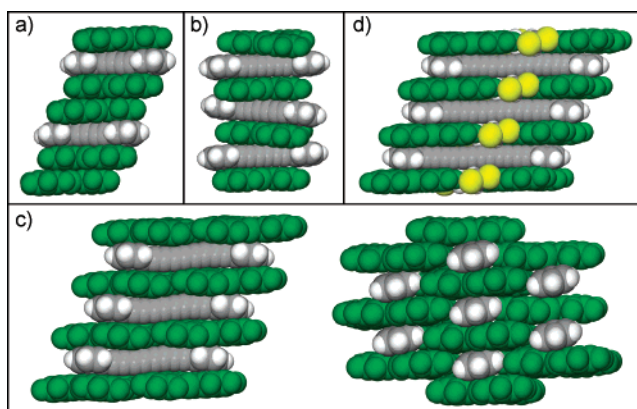
Figure 2. Supramolecular structure of **2** (a), **3** (b), **4** (c) and **5** (d) (color code: **1**: green; Ph(C≡C)$_n$Ph: C-atoms: gray, H-atoms: off-white; Cl-atoms: yellow). For the structure of **4** shown in c): left: view of a portion of the stacks; right: View of a portion of the molecular lattice showing how individual molecules of Ph(C≡C)$_4$Ph are separated from one another.

1 reside side by side and decorate the faces of juxtaposed molecules of polyyne. In the case of **5**, the increased length of the polyyne chain leads to the generation of a gap which is filled by two molecules of dichloromethane (Figures 1d and 2d). In all four structures, the arrangement of the adjacent stacks is such that the polyyne chains are entirely surrounded by molecules of **1** (Figure 2c). In **4** and **5**, the polyyne chain slightly

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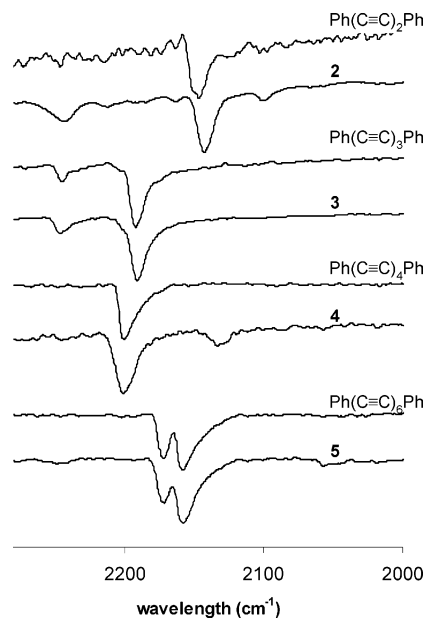
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Figure 3. IR spectra of **2**−**5**, Ph(C≡C)$_2$Ph, Ph(C≡C)$_3$Ph, Ph(C≡C)$_4$Ph, and Ph(C≡C)$_6$Ph, showing the acetylenic stretches.

deviates from linearity to exhibit an S-shaped conformation, which has been observed in the structural chemistry of such compounds.[25] Within the error of the X-ray measurements, the structures of the α,ω-diphenylpolyynes do not seem to be affected by their complexation to **1**, which is indicative of the weakness of the Hg−C interactions.

Spectroscopic Studies of the Adducts. The acetylenic stretches ($\nu_{C≡C}$) of **2**−**5** measured by IR spectroscopy are essentially identical with those of the free polyyne (Figure 3). The largest frequency difference is observed for **2**, whose $\nu_{C≡C}$ signal is red-shifted by 8 cm^{-1} when compared to that of Ph-(C≡C)$_2$Ph. To gather additional information concerning the electronic structure of the polyynes, adducts **2**−**5** have been studied by luminescence spectroscopy. The luminescence spectrum of **2** indicates complete quenching of the fluorescence and displays an emission whose energy and vibronic progression are identical with those reported for the phosphorescence of the pure diyne.[26] This observation is in agreement with a mercury heavy-atom effect, as observed in arene adducts of **1**.[16] Adducts **3**−**5** give rise to only faint emissions. Taken collectively, these spectroscopic studies corroborate the conclusion derived from the crystallographic studies and indicate that **1** acts as an innocent synthon which does not significantly alter the geometry or electronic structure of the polyyne.

Thermal Analysis of the Adducts. As indicated in the Introduction, the objective of this work is the discovery of a new method allowing for the stabilization of polyynes. Apart from **5**, which decomposes within a few days by loss of CH$_2$-Cl$_2$, adducts **2**−**4** are indefinitely stable under ambient conditions in a laboratory illuminated with fluorescent light. The stability of **3** and **4** is noteworthy, since Ph(C≡C)$_3$Ph and Ph(C≡C)$_4$Ph will rapidly decompose under the same conditions. To further assess the stabilization resulting from the complexation of the α,ω-diphenylpolyynes by **1**, we surveyed the thermal behaviors of the adducts by DSC/TGA and compared them to those of the corresponding pure α,ω-diphenylpolyynes. These measurements were carried out in air to obtain data that relate to the

behavior of the solids under ambient conditions. Taking into account the instability of Ph(C≡C)$_6$Ph and **5**, which loses solvent at room temperature, measurements were only carried out on Ph(C≡C)$_2$Ph, Ph(C≡C)$_3$Ph, and Ph(C≡C)$_4$Ph and their corresponding adducts **2**−**4** (Figure 4). According to the DSC measurements, the α,ω-diphenylpolyynes Ph(C≡C)$_2$Ph, Ph(C≡C)$_3$Ph, and Ph(C≡C)$_4$Ph melt at 92, 98, and 111 °C, as indicated by a detectable endotherm. These melting point values correspond to those reported in the literature,[4] which attests to the purity of our samples. For Ph(C≡C)$_2$Ph, melting is followed by a weight loss assigned to sublimation, which in principle should be endothermic. The DSC response, however, indicates the onset of an exotherm, suggesting that sublimation is accompanied by an exothermic polymerization. For Ph(C≡C)$_3$Ph and Ph(C≡C)$_4$Ph, melting is followed by a conspicuous exotherm, which begins at 135 °C for Ph(C≡C)$_3$Ph and 120 °C for Ph(C≡C)$_4$Ph. These temperatures most likely correspond to the advent of polymerization, since no mass loss is observed. The thermal behavior of the adducts is drastically different. For **2**, a slightly endothermic weight loss is observed at 250 °C, which probably corresponds to sublimation of Ph(C≡C)$_2$Ph and/or **1**. For adducts **3** and **4**, an exothermic decomposition is observed at about 240 °C. This decomposition is accompanied by a mass loss, which can be assigned to sublimation of some of the trinuclear mercury complex or to oxidative decomposition of the polyyne. Altogether, these DSC/TGA studies indicate that the adducts are more thermally stable than the respective free α,ω-diphenylpolyynes. In the case of Ph(C≡C)$_4$Ph, the stability range is increased by almost 120 °C under an oxidizing atmosphere. Similar conclusions could be derived by monitoring the acetylenic stretch of Ph(C≡C)$_4$Ph and **4** as a function of temperature in KBr. In the case of Ph(C≡C)$_4$Ph, the stretch disappears above 170 °C, while that in **4** persists beyond 250 °C.

Conclusion

Since binary solids containing directly adjacent polyynes have been shown to polymerize,[9,10] we propose that the increase in stability of α,ω-diphenylpolyynes in adducts **2**−**4** results from their entrapment and physical separation in a supramolecular lattice. Paradoxically, the supramolecular forces responsible for the formation of these adducts are weak and do not affect the structure of the polyynes. In contrast to previous efforts, our approach relies on the use of an innocent stabilizing unit which interacts with the polyyne via weak supramolecular interactions.

Experimental Section

General Considerations. Due to the toxicity of the mercury compounds discussed in these studies, extra care was taken at all times to avoid contact with solid, solution, and air-borne particulate mercury compounds. Most of the studies herein were carried out in well-aerated fume hoods. Atlantic Microlab, Inc., Norcross, GA, performed the elemental analyses. DSC/TGA experiments were performed with a TA Instruments Q600 SDT under an air purge at heating rates of 10−20 °C/min. All solvents were purchased commercially and used as provided for crystallizations. Ph(C≡C)$_2$Ph (1,4-diphenylbutadiyne (Strem)) was used as provided. Ph(C≡C)$_3$Ph, Ph(C≡C)$_4$Ph, and Ph(C≡C)$_6$Ph were synthesized using variations of reported literature procedures.[27] Luminescence spectra

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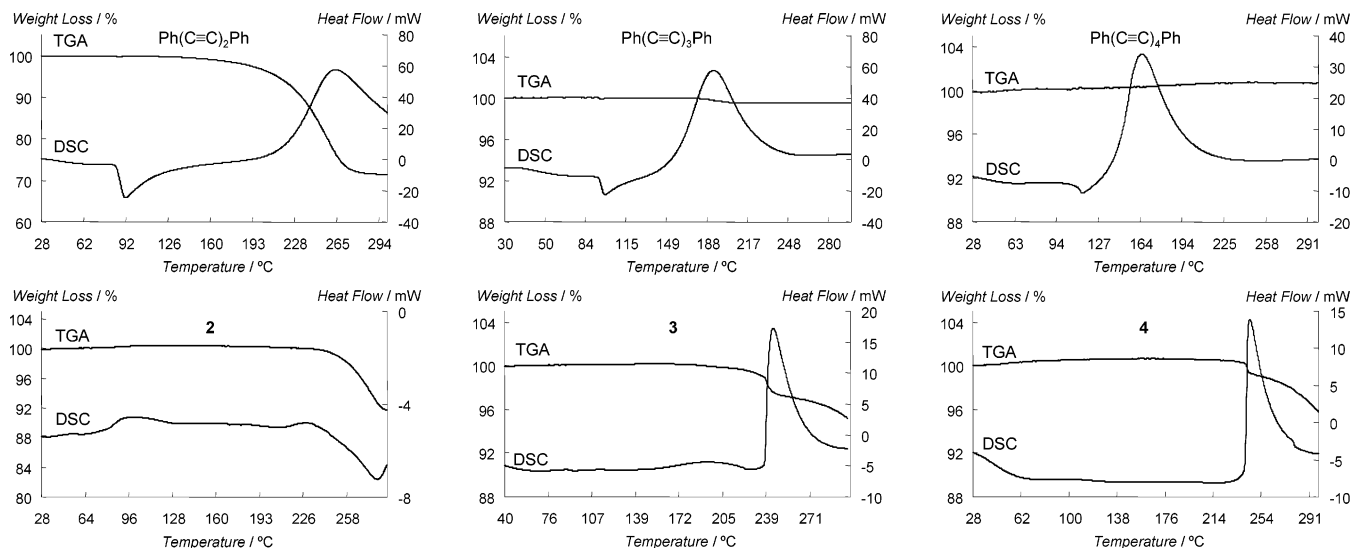
Figure 4. TGA and DSC traces for Ph(C≡C)$_2$Ph, Ph(C≡C)$_3$Ph, and Ph(C≡C)$_4$Ph (top) and **2**−**4** (bottom) acquired at a heating rate of 20.0 °C/min in an open pan.

were recorded with a SLM/AMINCO Model 8100 spectrofluorometer equipped with a xenon lamp. Low-temperature measurements were made in a cryogenic device of local design, and liquid nitrogen was used to obtain the 77 K measurements. IR spectra were recorded with a ATI-Mattson Genesis series FTIR spectrometer with the samples prepared as compressed KBr pellets. The bands were compared to reported values when available.[28] Variable-temperature measurements with **4** and Ph(C≡C)$_4$Ph were carried out with KBr pellets. The pellets were heated in an oven at the desired temperature for 20 min before each measurement. The temperature of the oven was increased by 20 °C increments until the band at 2200 cm^{-1} had disappeared.

Synthesis of 2−5. All compounds were prepared by mixing **1** with the appropriate polyyne in CH$_2$Cl$_2$ (5−15 mL). The reactions as well as the crystallizations were carried out in the dark. Crystals formed upon slow evaporation of the solvent (**2** and **3**) or upon cooling to −10 °C (**4** and **5**). In all cases, the crystals were separated from the mother liquor and rinsed with hexanes. Reagent quantities, yields, color of the crystals, elemental analysis results, and melting points are provided for each adduct hereafter.

Adduct **2**: **1** (24.5 mg, 0.024 mmol), Ph(C≡C)$_2$Ph (2.4 mg, 0.012 mmol). Yield: 22 mg, 80%. Colorless. Anal. Calcd for C$_{52}$H$_{10}$F$_{24}$-Hg$_6$: C, 27.22; H, 0.44. Found: C, 27.20; H, 0.30. mp 295 °C dec.

Adduct **3**: **1** (42.0 mg, 0.040 mmol), Ph(C≡C)$_3$Ph (10.0 mg, 0.042 mmol). Yield: 20.6 mg, 40%. Pale yellow. Anal. Calcd for

C$_{36}$H$_{10}$F$_{12}$Hg$_3$: C, 33.99; H, 0.79. Found: C, 34.05; H, 0.65. mp 299−300 °C dec.

Adduct **4**: **1** (47.0 mg, 0.045 mmol) and Ph(C≡C)$_4$Ph (6.0 mg, 0.024 mmol). Yield: 13 mg, 25%. Yellow. Anal. Calcd for C$_{56}$H$_{10}$F$_{24}$Hg$_6$: C, 28.72; H, 0.43. Found: C, 28.71; H, 0.33. mp 320 °C (decomp.).

Adduct **5**: **1** (40.0 mg, 0.039 mmol) and Ph(C≡C)$_6$Ph (6.0 mg, 0.020 mmol). Yield: 10 mg, 20%. Bright yellow. Elemental analysis was not feasible, as samples decomposed rapidly in the absence of solvent.

Single-Crystal X-ray Analysis. X-ray data for **2**−**4** were collected on a Bruker SMART 1000 CCD diffractometer, while data for **5** were collected on a Bruker SMART APEX CCD diffractometer, all using graphite-monochromated radiation from a Mo sealed X-ray tube (Kα = 0.701 73 Å). Specimens of suitable size were mounted on glass loops with mineral oil. The structures were solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinement on F^2 using the SHELXTL/PC package (version 5.1) allowed location of the remaining non-hydrogen atoms.

Supporting Information Available: Tables and figures giving additional spectroscopic and crystallographic data; crystallographic data are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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