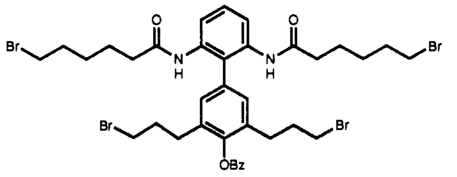
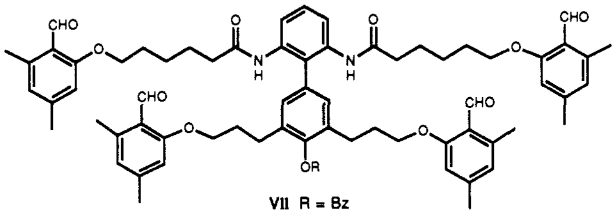
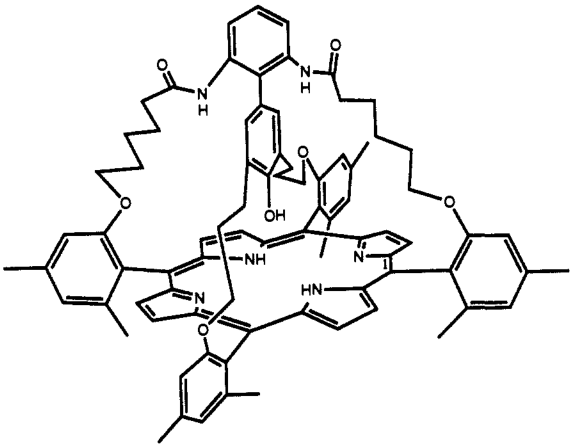
(74%). Reaction of V with 6-bromohexanoyl chloride (in THF/pyridine at -60 °C warming to 10 °C) followed by reaction of the resultant diamide VI with the sodium salt of 2-hydroxy-4,6-dimethylbenzaldehyde[2] (THF/HMPA at 35 °C for 96 h) yielded tetraaldehyde VII (42%). Removal of the *O*-benzyl blocking group with CF_3CO_2H (55 °C for 6 h, 70% yield) and reaction of the resultant phenolic tetraaldehyde VIII with pyrrole, following the method of Lindsey,[3] provided the desired pendant-capped porphyrin IXH_3 in 7% yield (two protons residing on porphyrin pyrrole nitrogens and the third proton on the phenolic substituent). The pendant porphyrin was characterized by ^1H NMR, UV/vis, IR, and mass spectroscopy.[4]



VI



VII R = Bz
VIII R= H



IXH_3

Insertion of iron(III) into IXH_3 to provide $(IX)Fe^{III}$ was carried out after the method of Kobayashi.[5] That the Fe(III) moiety of $(IX)Fe^{III}$ is axially coordinated to the phenoxy substituent of the cap was established from IR, UV/vis, ^1H NMR, and laser desorption mass spectroscopy. In the IR spectra the characteristic phenolic O–H absorption at 3450 cm^{-1} of IXH_3 is lost on conversion to $(IX)Fe^{III}$. The UV/vis spectrum of $(IX)Fe^{III}$ exhibits absorbance maxima [$CHCl_3$, λ_{max}, nm ($\epsilon \times 10^4$ M^{-1} cm^{-1}), 325 (3.3), 420 (13.5), 490 (1.1), 552 (0.66), 608, 653] comparable to the spectrum of the analogous phenoxy-ligated (tetraphenylporphinato)Fe(III) [$(TPP)Fe^{III}(OC_6H_5)$].[6] The high-field ^1H NMR spectrum is consistent[6-8] with the above structural assignment [($CDCl_3$, 500 MHz, 23 °C), δ 13.4, 13.1, 11.9, 11.6 (meso-phenyl, meta Hs), 82.6 (β-pyrrolic Hs), 122.4 (Hs meta to Fe^{III}–O bond)]. The spectrum of $(IX)Fe^{III}$ shows the distinctive resonance pattern that is characteristic for a high spin ($S = {}^5/_2$), five-coordinate iron(III) formulation. The line width of the pyrrole resonance (1796 Hz) is consistent with an oxygen donor occupying the fifth coordination site. Moreover, the spectrum of $(IX)Fe^{III}$ shows the distinctly characteristic resonance at 122 ppm corresponding to the axially coordinated phenolate meta resonance. Additionally, the composition of $(IX)Fe^{III}$ was verified by high-resolution laser desorption MS [calcd for $(C_{82}H_{79}N_6OFe + Na)^+$ *m/e* 1338.518, found $(M + Na)^+$ *m/e* 1338.546], which showed no proton on the phenolic oxygen and the absence of any other axial ligand (such as Cl^-).

Chemical properties of $(IX)Fe^{III}$ as well as other metal complexes formed from IXH_3 will be reported at a latter date. The obvious challenge is to synthesize a pendant cap tetraphenylporphyrin that secures in place and protects a S^- ligand. The accomplishment of such a synthesis and the studies that would ensue could be critical to the understanding of the mechanism of cytochrome P-450. Work toward this end is in progress in our laboratory.

Acknowledgment. This investigation was supported by a grant from the National Institutes of Health. High-resolution mass spectrometry was performed by Prof. Charles L. Wilkins, Department of Chemistry, University of California at Riverside.

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[4] 1-D ^1H NMR decoupling and 2-D ^1H NMR COSY experiments were used to assign the chemical shifts. The amide strap carbons are labeled α–ϵ and the propoxy strap carbons are labeled 1–3. ^1H NMR ($CDCl_3$, 300 MHz, $CHCl_3$ assigned at δ 7.24) δ −2.18 (br s, 2 H, pyrrolic NH), −0.41 to −0.36 (m, 4 H, C-1 Hs), 0.14–0.19 (m, 4 H, δ-CH_2), 0.46–0.53 (m, 4 H, γ-CH_2), 0.55–0.63 (m, 8 H, C-2 Hs and β-CH_2), 1.77 (t, 4 H, $J = 7.0$ Hz, α-CH_2), 1.85, 2.18, 2.61, 2.64 (s, 6 H each, CH_3s), 3.54 (t, 4 H, $J = 7.3$ Hz, ϵ-CH_2), 3.77 (t, 4 H, $J = 5.0$ Hz, C-3 Hs), 5.73, 6.14, 6.88, 7.03, 7.05, 7.21 (s, 2 H each, amide NH and meso phenyl Hs), 7.06 (t, 1 H, $J = 8.4$ Hz, H meta to amide), 7.67 (d, 2 H, $J = 8.4$ Hz, H ortho to amide), 8.67 (d, 4 H, $J = 4.8$ Hz, β-pyrrolic Hs), 8.70 (d, 4 H, $J = 4.8$ Hz, β-pyrrolic Hs); UV/vis ($CHCl_3$) λ_{max}, nm ($\epsilon \times 10^4$ M^{-1} cm^{-1}), 402 (sh), 420 (32.2), 512 (12.5), 551 (3.0), 589 (3.0), 643 (0.5); IR ($CHCl_3$) ν, 3450 (br, O–H), 3415 (m, amide NH), 3340 (w, pyrrole NH), 1680 (s, C=O) cm^{-1}; FABMS calcd for $C_{82}H_{82}N_6O_4$ *m/e* 1262.62, found *m/e* 1263.

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$[ECd_8(E'Ph)_{16}]^{2-}$ Cluster Chemistry (E, E' = S, Se, Te)

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We have established systematic entry to the chemistry of the class of clusters formulated $[ECd_8(E'Ph)_{16}]^{2-}$ (**1**), E, E' = S, Se, Te. This class adds to the two others we have described, namely, $[E_4M_{10}(E'Ph)_{16}]^{4-}$ (**2**), M = Zn, Cd,[1,2] and $[S_4Cd_{17}(SPh)_{28}]^{2-}$ (**3**).[3]

Complexes $[SCd_8(SPh)_{16}]^{2-}$ (**1a**), $[SCd_8(SePh)_{16}]^{2-}$ (**1b**), $[SeCd_8(SePh)_{16}]^{2-}$ (**1c**), $[TeCd_8(SePh)_{16}]^{2-}$ (**1d**), and $[SCd_8(TePh)_{16}]^{2-}$ (**1e**) can be synthesized by self-assembly of $E'Ph^-$ (E' = S, Se, Te), CdI_2, and Na_2E or NaEH (E = S, Se, Te) in the composition range 0.2 ≤ E/Cd ≤ 0.3, 1 < E'Ph/Cd < 3, in alcohols/acetonitrile.[4] Crystalline compounds isolated from these reactions and characterized by correct elemental analysis and/or Cd NMR (see below) include the following: **1b** with Me_4N^+,

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[4] $(Et_4N)_2\cdot$**1b**: A deoxygenated solution of NaSePh (15.5 mmol, in ethanol (70 mL)/acetonitrile (70 mL)) was treated with solutions of CdI_2 (6.4 mmol) in acetonitrile (20 mL), Na_2S (1.6 mmol) in methanol (20 mL), and Et_4NCl (2.5 mmol) in acetonitrile (20 mL), yielding a colorless solution. After stripping of all solvent, the colorless solids were extracted with water at 80 °C and ethanol at ambient temperature, then dissolved in acetonitrile at 20 °C, and filtered, and $(Et_4N)_2[SCd_8(SePh)_{16}]$ (ca. 38%, on Cd) crystallized by storage at 0 °C. Anal. $Cd_8SSe_{16}N_2C_{106}H_{120}$, C, H, N, Cd.

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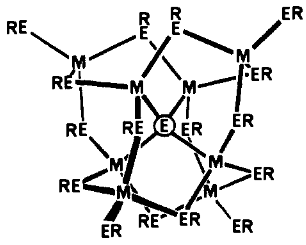

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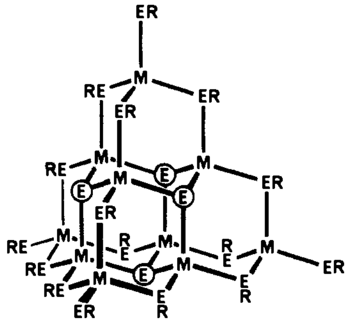

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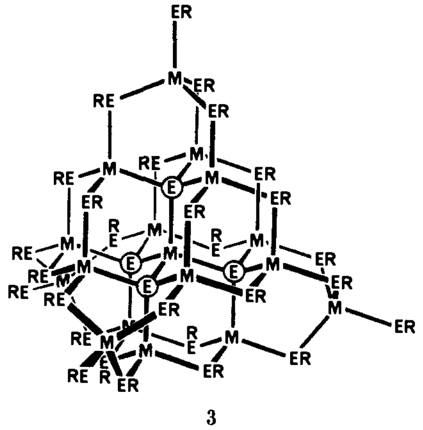

3

Ph_4E^+ (E = P, As), Bu_4N^+, $PhCH_2NR_3^+$ (R = Me, Et); **1c** with Me_4N^+, Et_4N^+; **1d** with Et_4N^+; **1e** with Et_4N^+. $(Me_4N)_2$·**1b** is also formed by reaction of $[Cd_4(SePh)_{10}]^{2-}$ in acetonitrile with 0.5 equiv of Na_2S or NaSH (methanol) or 1 equiv of S_8, at room temperature, and by reaction of $Cd(SePh)_2$ in DMF with Na_2S or NaSH.

Most of these crystalline products did not diffract, or were twinned or otherwise unsuitable for diffraction analysis, and confirmation of the structure **1** was finally achieved by diffraction on crystals of $(Et_4N)_2$·**1b**·(DMF).[5] The structure of **1b** is shown in Figure 1. The central S^{2-} ion is coordinated to four inner Cd^i atoms (Cd1–Cd4), each connected through three doubly bridging SePh ligands (Se^b) to outer Cd^o atoms (Cd5–Cd8) with terminal SePh ligands (Se^t). All atoms have tetrahedral or part tetrahedral coordination. No crystallographic symmetry is imposed on **1b**, but the core without substituents has virtual symmetry *T*, which is approximated to a lesser extent by the bridging SePh ligands. Dimension statistics[6] reveal the relatively small distortions from the idealized structure, and the expected gradations of bond length, $Cd^o–Se^b \gtrsim Cd^i–Se^b > Cd^o–Se^t > S–Cd^i$. The structure can be conveniently described by its constituent polyhedra: the Cd atoms constitute a ditetrahedron (tetracapped tetrahedron), with Cd–Cd 4.16 (18, 0.05) Å,[6] while the $(Se^b)_{12}$ polyhedron, which could be a cuboctahedron or icosahedron,[7] is close to an icosahedron for which Se–Se = 4.3 (30, 0.2) Å. Thus the structure can be described as *centro*-S-*tetrahedro*-Cd^i_4-*icosahedro*-$(\mu\text{-SePh})_{12}$-*tetrahedro*-Cd^o_4-*tetrahedro*-$(SePh)_4$. An alternative description places four Cd^i inside and four Cd^o outside the triangular faces of an $(Se^b)_{12}$ icosahedron. Configurational isomerism is allowed at each pyramidal (μ-SePh) ligand, and the array of $Se–C_\alpha$ vectors over the surface of the icosahedron is the most symmetrical allowed, in which the C_α atoms approximate a cuboctahedron.[8]

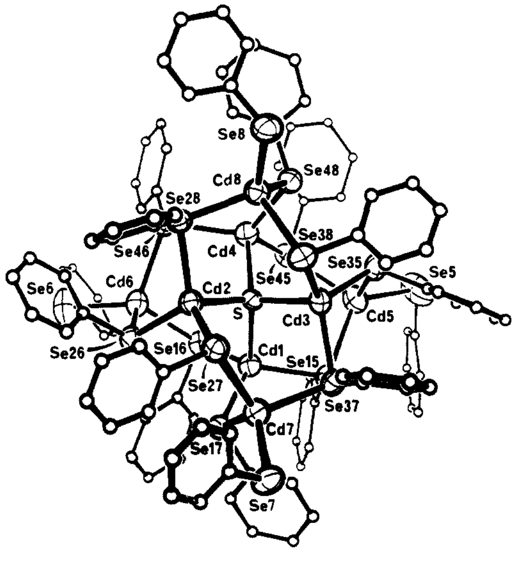

Figure 1. View of $[SCd_8(SePh)_{16}]^{2-}$ (**1b**) along one of the pseudo-2-fold axes. Ellipsoids for the Cd, S, and Se atoms are at 40% probability.

The ^{113}Cd and ^{77}Se NMR spectra[9] of **1b** in DMF (slow exchange throughout the temperature range 260–340 K) confirm the integrity of the complex in solution. The Cd^i and Cd^o resonances occur at 582 and 522 ppm, respectively (300 K); coupling satellites due to $^2J(Cd^i–Cd^o)$ = 59 Hz are resolved on both lines, while isotope coupling $^2J(^{113}Cd^i–^{111}Cd^i)$ of smaller magnitude has not yet been resolved. The Se^b and Se^t resonances occur at −1.3 and −65.7 ppm, respectively (300 K). Satellites due to $^1J(Cd^o–Se^t)$ = 175 Hz, $^1J(Cd^o–Se^b)$ = 171 Hz, and $^1J(Cd^i–Se^b)$ = 119 Hz occur in both the Cd and Se spectra. The NMR data for the other members of the class are as follows: **1a** $\delta(Cd^i)$ = 608, $\delta(Cd^o)$ = 567 ppm, $^2J(Cd^i–Cd^o)$ = 42 Hz; **1c**, $\delta(Cd^i)$ = 553, $\delta(Cd^o)$ = 513 ppm, $^2J(Cd^i–Cd^o)$ = 59 Hz, $^1J(Cd^o–Se)$ = 143 Hz; **1d**, $\delta(Cd^i)$ = 461, $\delta(Cd^o)$ = 526 ppm (this compound is unstable in solution); **1e**, $\delta(Cd^i)$ = 549, $\delta(Cd^o)$ = 442 ppm.

We have investigated a variety of transformations involving **1**. The conversion of $[S_4Cd_{10}(SePh)_{16}]^{4-}$ (**2b**) to **1b** occurs on standing in deoxygenated DMF solution, requiring 2 weeks at room temperature: homologous **2a** to **1a** conversion is effected also by reaction with metal ions such as Pb^{2+} and Cd^{2+} and by irradiation with unfiltered UV light in DMF or acetonitrile. Reaction of **2a** with excess PhSeSePh yields **1b**, and **3** transforms to **1a** on standing in DMF solution. All of these observations are consistent with high stability for **1**. The reverse **1** → **2** conversion can be effected by reaction of **1b** with excess PhS^- to yield **2a**. Terminally substituted derivatives of structure **1** have been characterized: reaction of **1b** in DMF with CdX_2 (X = Br or I) at 20 °C gen-

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(5) Crystallography: $(Et_4N)_2$·**1b**·DMF, $Cd_8SSe_{16}N_3OC_{115}H_{127}$, *M* = 3761.9, monoclinic space group $P2_1/n$, *a* = 19.67 (1) Å, *b* = 32.172 (9) Å, *c* = 20.04 (1) Å, β = 90.42°, *V* = 12679 (10) $Å^3$, *Z* = 4, D_{calcd} = 1.97 g cm^{-3}; 6668 unique reflections, Mo Kα radiation, to 2θ = 32°, crystal decay 60% (corrected); solution by direct methods, least-squares refinement with Cd, Se, and S anisotropic, and the SePh substituents as constrained planar groups; *R* = 0.038, R_w = 0.047 for 4412 observed reflections. The cluster **1b** is separated in the crystal from the cations and DMF. Full details of this structure will be published separately.

(6) Dimension statistics (Å, deg) are presented as mean of the independent values (sample size, standard deviation of the *sample*): $S–Cd^i$, 2.519 (4, 0.007); $Cd^i–Se^b$, 2.638 (12, 0.008); $Se^b–Cd^o$, 2.69 (12, 0.02); $Cd^o–Se^t$, 2.572 (4, 0.007); $Cd^i–S–Cd^i$, 110 (6, 1); $S–Cd^i–Se^b$, 104 (12, 2); $Se^b–Cd^i–Se^b$, 115 (12, 2); $Cd^i–Se^b–Cd^o$, 104 (12, 1); $Se^b–Cd^o–Se^b$, 106 (12, 2); $Se^b–Cd^o–Se^t$, 113 (12, 4).

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(8) As previously analyzed,[7] the edges of the cuboctahedron occur as 12 at 4.6 (2) Å and 12 at 6.4 (2) Å.

(9) Chemical shift references are aqueous $Cd(NO_3)_2$ (0.1 M), set as δ_{Cd} = 0.0 ppm (0.1 M aqueous $Cd(ClO_4)_2$ resonates at 4 ppm on this scale), and aqueous Na_2SeO_3, set as $\delta(Se)$ = 1253 ppm relative to $\delta(Se)$ = 0 ppm for neat Me_2Se.

erates $[SCd_8(SePh)_{12}Br_4]^{2-}$ (**1f**) ($\delta(Cd^i) = 579$, $\delta(Cd^o) = 493$ ppm, ${}^2J(Cd^i{-}Cd^o) = 47$ Hz) or $[SCd_8(SePh)_{12}I_4]^{2-}$ (**1g**) ($\delta(Cd^i) = 578$, $\delta(Cd^o) = 442$ ppm), while the crystal structure of $(Me_4N)_2$-$[SCd_8(SPh)_{12}Cl_4]$, synthesized by self-assembly, has been completed. Details of all reactions and structures will be reported separately.

In metal chalcogenide systems the cluster framework **1** has been observed previously only in $[ClZn_8(SPh)_{16}]^-$ (**1h**)[7] and in the nonmolecular crystal structure of ${}^3_\infty[\{SCd_8(SBu^s)_{12}\}(CN)_{4/2}]$.[10] Reproducible synthesis is not yet available for either of these compounds, and therefore the main significance of the results reported here is the establishment of the synthetic and interconversion reactions.

We are applying the structural and dynamic principles embodied in these results to questions of formation and structure for cadmium chalcogenide colloids in a variety of media[11-13] and to peptide-coated cadmium sulfide nanocrystallites generated biologically.[14,15]

Acknowledgment. This research is supported by the Australian Research Council, the National Research Fellowships Scheme (K.J.F.), and a postgraduate student award (G.S.H.L.). The assistance of Dr. A. D. Rae with the program RAELS is gratefully acknowledged.

Supplementary Material Available: Atomic positional and thermal parameters, bond lengths, bond angles, and torsional angles for $(Et_4N)_2$·**1b**·(DMF) (15 pages). Ordering information is given on any current masthead page.

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Bis[phenyl[(perfluoroalkanesulfonyl)oxy]iodo]acetylene, $PhI^+C\equiv CI^+Ph\cdot 2R_FSO_3^-$, and 1,4-Bis[phenyl[(perfluoroalkanesulfonyl)oxy]iodo]-1,3-butadiyne, $PhI^+C\equiv C{-}C\equiv CI^+Ph\cdot 2R_FSO_3^-$

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There is considerable current interest and research activity in tricoordinate iodine(III) compounds.[1] The latest members of the family of multicoordinate iodine species, alkynyl(phenyl)iodonium salts, **1**, have become valuable reagents in organic chemistry. They

$$\underset{\mathbf{1}}{RC\equiv CI^+Ph\cdot X^-} \qquad \underset{\mathbf{2}}{XC\equiv C{-}C\equiv CX}$$

serve as precursors to novel alkynyl esters,[2] undergo cyclopentene annulations[3] and coupling with vinylcopper reagents,[4] and serve as progenitors of a unique vinyliodinane species[5] and of microbiocides.[6] They also function as alkynylating agents in both organic[7] and organometallic[8] chemistry.

Likewise, there is surging interest in functionalized acetylenes and diacetylenes (1,3-diynes), **2**, from both the perspective of their rich chemistry[9] and the unique properties of their homopolymers.[10] Therefore, in the present communication we report the ready preparation, physical and spectral properties, and some preliminary chemistry, of two new, unique alkynyliodonium species; the bisfunctionalized acetylene **3**, and the diacetylene **4**.

$$PhI^+C\equiv CI^+Ph\cdot 2R_FSO_3^- \qquad PhI^+C\equiv C{-}C\equiv CI^+Ph\cdot 2R_FSO_3^-$$

3a, $R_F = CF_3$ **4a**, $R_F = CF_3$
3b, $R_F = n\text{-}C_4F_9$ **4b**, $R_F = n\text{-}C_4F_9$

Addition of a CH_2Cl_2 solution of bis-tinacetylene **5** to a cooled suspension of the appropriate mixed iodonium sulfonate[11] **6** in CH_2Cl_2 under N_2 results in the formation of a white precipitate (eq 1). The precipitate is filtered and washed with cold ether

$$\underset{\mathbf{5}}{n\text{-}Bu_3SnC\equiv CSnBu_3\text{-}n} + 2PhI^+CN\cdot R_FSO_3^-$$

6a, $R_F = CF_3$
6b, $R_F = n\text{-}C_4F_9$

$$\xrightarrow[-2n\text{-}Bu_3SnCN]{CH_2Cl_2,\ -30\ to\ -20\ ^\circ C,\ N_2} PhI^+C\equiv CI^+Ph\cdot 2R_FSO_3^- \quad (1)$$

3a, $R_F = CF_3$
3b, $R_F = n\text{-}C_4F_9$

resulting in the desired product **3** as a white microcrystalline solid.[12] The bisiodonium fluorosulfonates **3a** and **3b** are stable in the solid state at room temperature for several days and in a refrigerator for weeks; however, they react in a matter of minutes to hours with liberation of iodobenzene in most polar solvents (H_2O, CH_3OH, C_2H_5OH, CH_3CN, etc.). The corresponding tosylate or mesylate salts could not be isolated as stable compounds.

Likewise in an exactly analogous manner the bisiodonium diacetylene **4** may be prepared (eq 2). However, whereas adducts

$$\underset{\mathbf{7}}{Me_3SnC\equiv C{-}C\equiv CSnMe_3} + 2PhI^+CN\cdot 2R_FSO_3^-$$

6a, $R_F = CF_3$
6b, $R_F = n\text{-}C_4F_9$

$$\xrightarrow[-2Me_3SnCN]{CH_2Cl_2,\ -30\ ^\circ C,\ N_2} PhI^+C\equiv C{-}C\equiv CI^+Ph\cdot 2R_FSO_3^- \quad (2)$$

4a, $R_F = CF_3$
4b, $R_F = n\text{-}C_4F_9$

3 are stable, the bisiodonium diacetylene analogues **4** decompose

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(12) For **3a**: yield 81%; mp 127-128 °C dec; IR (CCl_4) 3095, 1581, 1560, 1281, 1237, 1217, 1169, 1025, 983 cm^{-1}; ^1H NMR (CD_3CN) δ 7.55-7.65 (m, 2 H), 7.7-7.8 (m, 1 H), 8.1-8.2 (m, 2 H); ^{13}C NMR (CD_3CN) δ 51.84 ($C\equiv C$), 120.5 (quart, $J = 318$ Hz, CF_3) 123.65, 133.84, 134.61, 136.18 (Ph); ^{19}F NMR (CD_3CN) δ −78.95 (s, CF_3). Anal. Calcd for $C_{16}H_{10}I_2O_6S_2F_6$: C, 26.32; H, 1.38; S, 8.78. Found: C, 26.27; H, 1.39; S, 8.84. For **3b**: yield 55%; mp 101-102 °C dec; IR (CCl_4) 3090, 1559, 1471, 1446, 1356, 1226, 1206, 1136, 1057, 983 cm^{-1}; ^1H NMR (CD_3CN) δ 7.55-7.65 (m, 2 H), 7.75-7.85 (m, 1 H), 8.1-8.2 (m, 2 H); ^{13}C NMR (CD_3CN) δ 50.91 ($C\equiv C$), 100-110 (m, C_4F_9), 118.72, 133.82, 134.57, 136.25 (Ph); ^{19}F NMR (CD_3CN) δ 4.75 (m, CF_2), −2.25 (m, CF_2), −6.68 (m, CF_2), −81.21 (m, CF_3).

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