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]

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Supplementary Material Available: Atomic positional and thermal parameters, bond lengths, bond angles, and torsional angles for $(Et_4N)_2\cdot$**1b**$\cdot$(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**.

$$\underset{\substack{\mathbf{3a},\ R_F = CF_3\\ \mathbf{3b},\ R_F = n\text{-}C_4F_9}}{PhI^+C{\equiv}CI^+Ph\cdot 2R_FSO_3^-} \qquad \underset{\substack{\mathbf{4a},\ R_F = CF_3\\ \mathbf{4b},\ R_F = n\text{-}C_4F_9}}{PhI^+C{\equiv}C{-}C{\equiv}CI^+Ph\cdot 2R_FSO_3^-}$$

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

$$\underset{\mathbf{5}}{n\text{-}Bu_3SnC{\equiv}CSnBu_3\text{-}n} + \underset{\substack{\mathbf{6a},\ R_F = CF_3\\ \mathbf{6b},\ R_F = n\text{-}C_4F_9}}{2PhI^+CN\cdot R_FSO_3^-} \xrightarrow[-2n\text{-}Bu_3SnCN]{CH_2Cl_2,\ -30\ \text{to}\ -20\ ^\circ C,\ N_2} \underset{\substack{\mathbf{3a},\ R_F = CF_3\\ \mathbf{3b},\ R_F = n\text{-}C_4F_9}}{PhI^+C{\equiv}CI^+Ph\cdot 2R_FSO_3^-} \quad (1)$$

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

$$\underset{\mathbf{7}}{Me_3SnC{\equiv}C{-}C{\equiv}CSnMe_3} + \underset{\substack{\mathbf{6a},\ R_F = CF_3\\ \mathbf{6b},\ R_F = n\text{-}C_4F_9}}{2PhI^+CN\cdot 2R_FSO_3^-} \xrightarrow[-2Me_3SnCN]{CH_2Cl_2,\ -30\ ^\circ C,\ N_2} \underset{\substack{\mathbf{4a},\ R_F = CF_3\\ \mathbf{4b},\ R_F = n\text{-}C_4F_9}}{PhI^+C{\equiv}C{-}C{\equiv}CI^+Ph\cdot 2R_FSO_3^-} \quad (2)$$

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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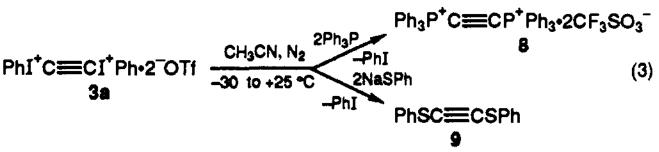
above −10 to −20 °C and hence *all* handling must be done at low temperatures.[13]

The bisiodonium adducts **3** and **4** were characterized by IR and multinuclear NMR spectroscopy, and where stable, (i.e., **3a**) by microanalysis.[12,13] Specifically, the infrared indicated only aromatic C–H stretching and absorptions highly characteristic of triflates and nonaflates.[14] The presence of the perfluoroalkanesulfonate groups was confirmed by ^{19}F NMR. In the case of **4a** a characteristic[9] conjugated C≡C absorption occurs at 2070 cm^{-1}. The ^1H NMR spectra had the typical 2:1:2 aromatic signals highly characteristic of the phenyl group in iodonium salts. Most important, the ^{13}C NMR spectra were all consistent with the proposed structures.

The title compounds **3** and **4** may be looked upon as novel, "stabilized" forms[15,16] of C_2 and C_4, respectively. Moreover, in analogy with the behavior of **1** toward nucleophiles[2] they should be premier C_2 and C_4 transfer agents and thereby serve as progenitros par exellence for difunctionalized acetylenes and diacetylenes.[9] Indeed, reaction of **3a** with 2 equiv of either Ph_3P or NaSPh in CH_3CN at −30 to +25 °C results in the corresponding difunctional acetylenes **8**[17] and **9**,[18] respectively (eq 3). Likewise, **4a** reacts with Ph_3P and NaSPh but the resulting diphosphonium-1,3-diyne is unstable and only product **10**[19] may be isolated (eq 4).



(3)

$$\underset{\mathbf{4a}}{PhI^+C{\equiv}C{-}C{\equiv}CI^+Ph{\cdot}2CF_3SO_3^-} + 2NaSPh \xrightarrow[-PhI,\ -NaOTf]{CH_3CN,\ -30\ ^\circ C} \underset{\mathbf{10}}{PhSC{\equiv}C{-}C{\equiv}CSPh} \quad (4)$$

In conclusion, we have discovered a simple procedure for the preparation of the hitherto unknown diiodonium acetylenes **3** and diiodonium diacetylenes **4**. These adducts readily react with nucleophiles resulting in C_2 and C_4 transfer and the concomitant formation of difunctional acetylenes and difunctional 1,3-diynes, respectively. Further chemistry and uses of these novel diiodonium acetylenes will be the subject of future reports.

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(13) Compound **4a** was isolated by filtration at −50 °C under N_2 and, upon washing with *cold* ether, gave 85% of **4a** as a white microcrystalline solid that turned to a black tar between −15 and −10 °C. *All* spectra were obtained at −35 °C: IR (CH_2Cl_2) 3051, 2070 (C≡C), 1444, 1382, 1260, 1173, 1030 cm^{-1}; ^1H NMR (CD_3CN) δ 7.7–7.8 (m, 2 H), 7.9–8.0 (m, 1 H), 8.3–8.4 (m, 2 H); ^{13}C NMR (CD_3CN) δ 33.11 (C≡C), 84.01 (C≡C), 120.5 (quart, J_{CF} = 318 Hz, CF_3), 129.75, 131.90, 132.77, 134.47 (Ph); ^{19}F NMR (CD_3CN) δ −78.61 (s, CF_3). The corresponding nonaflate **4b** and tosylate and mesylate salts were too unstable to isolate and to obtain spectral data.

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(17) For **8**: 99% yield; mp 218–220 °C dec; IR (CCl_4) 3059, 1584, 1485, 1285, 1240, 1027 cm^{-1}; ^1H NMR (CD_3CN) δ 7.65–7.74 (m, 2 H), 7.75–7.84 (m, 2 H), 7.9–8.0 (m, 1 H); ^{31}P NMR ($CDCl_3$) δ 21.16; ^{19}F NMR (CD_3CN) δ −78.65 (s, CF_3); ^{13}C NMR (CD_3CN) δ 114.9 (m, C≡C), 130.4, 134.25, 135.95, 137.9 (all m, Ph). Anal. Calcd for $C_{40}H_{30}P_2F_6S_2O_6$: C, 56.74; H, 3.57; S, 7.57. Found: C, 56.39; H, 3.82; S, 7.63.

(18) For **9**: 66%, oil; IR (neat) 2957, 1579, 1477, 1439, 1298, 1072, 1023, 998, 899, 735, 687 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.2–7.4 (m, 3 H), 7.5–7.6 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 87.98 (C≡C), 126.03, 127.11, 129.28, 133.27 (Ph).

(19) For **10**: 67%, oil; IR (neat) 3059, 2193 (C≡C), 1571, 1471, 1438, 1057, 1014, 997, 733, 686 cm^{-1}; ^1H NMR (CD_3Cl) δ 7.20–7.55 (m, Ph); ^{13}C NMR ($CDCl_3$) δ 71.72 (C≡C), 127.07 (C≡C), 127.41, 127.48, 129.03, 129.47 (Ph). This compound darkens and decomposes upon standing for several hours at room temperature.

Electron-Transfer Communication between a Redox Polymer Matrix and an Immobilized Enzyme: Activity of Nitrate Reductase in a Viologen–Acrylamide Copolymer

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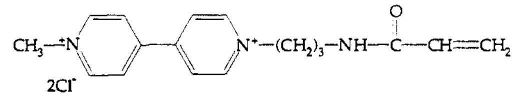
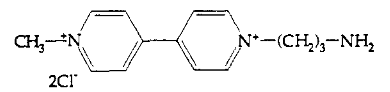
Long-range electron transfer to the active sites of oxidoreductase enzymes has been the subject of recent extensive research activities.[1-4] It has been shown that modification of the protein backbone by electron carriers allows electron transfer across the protein structure to the active site. Also, electrostatic association of glucose oxidase to a redox polyelectrolyte enabled electron-transfer communication between the redox polymer and the enzyme. Here we report on the long-range electron transfer to nitrate reductase through immobilization of the biocatalyst in a functionalized polymer matrix.

The monomer *N*-methyl-*N'*-(acrylamidopropyl)-4,4'-bipyridinium (**1**) is prepared by reacting *N*-methyl-*N'*-(aminopropyl)-4,4'-bipyridinium (**2**)[5] with *N*-(acryloyloxy)succinimide (**3**).[6] Nitrate reductase, EC 1.9.6.1 from *Aspergillus niger*, 0.2 mg, 0.1 unit, is polymerized[7] in an aqueous solution, pH = 7.5, that includes nitrate (7 × 10^{-3} M), **1** (113.3 mg), acrylamide (375 mg), and 20 mg of *N*,*N'*-methylenebis(acrylamide). The resulting copolymer gel is washed thoroughly until no free **1** is detectable in the aqueous phase by dithionite reduction. The immobilized enzyme retains 55% of the native enzyme activity. By measuring the amount of **1** that is eliminated during the purification of the gel, we estimate the ratio **1**:acrylamide in the polymer gel to be ca. 1:35. Introduction of dithionite into an aqueous suspension of the functionalized gel beads results in the blue coloration of the gel pieces. Alternatively, this can be achieved by illuminating the gel beads in the presence of ruthenium(II) tris(bipyridine) ($Ru(bpy)_3^{2+}$) and ethylenediaminetetraacetic acid disodium salt ($EDTANa_2$), as sacrificial electron donor, at pH = 7.44. The blue color persists in the polymer for days, and no leakage of the blue color to the aqueous phase is observed. These observations imply that the bipyridinium functionalized acrylamide copolymer is reducible by dithionite and by the photochemical process.

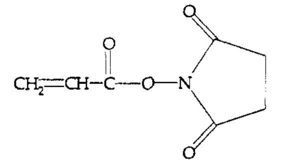
(1)



(2)



(3)



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