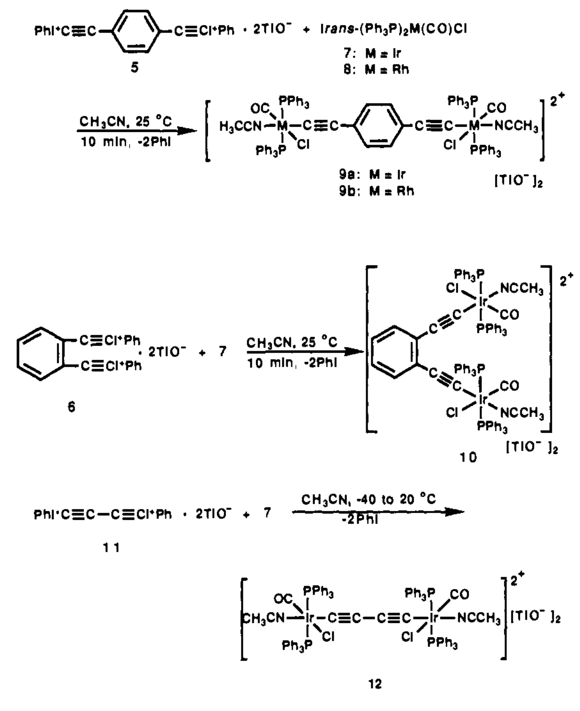
Table I. Physical and Spectral Properties of Complexes **9a**,**b**, **10**, and **12**

compd	yield, %	mp, °C	IR[c]	^{1}H NMR[d]	^{13}C NMR[d]	^{31}P NMR[e]	^{19}F NMR[f]
9a[a]	85	199–201, dec	3058, 2156 (C≡C), 2100 (CO), 1264, 1152, 1032	7.9–8.0 (24 H), 7.5–7.6 (36 H), 6.82 (4 H), 1.66 (6 H)	155.9 (CO, $^2J_{CP}$ = 6 Hz), 135.4 ($^2J_{CP}$ = 5 Hz), 133.3, 131.9, 129.8 ($^3J_{CP}$ = 5 Hz), 128.1 ($^1J_{CP}$ = 30 Hz), 125.3, 121.6, 108.7 (C-β), 56.3 (C-α, $^2J_{CP}$ = 12 Hz), 3.8 (CH$_3$CN)	−9.85	−79.1
9b[a]	73	105–106, dec	3061, 2147 (C≡C), 2122 (CO), 1267, 1154, 1031	7.9–8.0 (24 H), 7.5–7.6 (12 H), 7.4–7.5 (24 H), 6.78 (4 H)	g	19.74 ($^1J_{Rh,P}$ = 72.3 Hz)	−78.8
10[a]	65	165–168, dec	3062, 2124 (C≡C), 2093 (CO), 1224, 1154, 1031	7.8–7.9 (24 H), 7.2–7.4 (36 H), 7.0 (4 H), 1.64 (6 H)	155.3 (CO, $^2J_{CP}$ = 7 Hz), 136.6, 135.3 ($^2J_{CP}$ = 5 Hz), 133.0, 129.7 ($^3J_{CP}$ = 5 Hz), 127.6 ($^1J_{CP}$ = 30 Hz), 127.4, 122.2, 122.1 (OTf, $^1J_{CF}$ = 321 Hz), 109.1 (β-C, $^3J_{CP}$ = 4 Hz), 60.3 (α-C, $^2J_{CP}$ = 12 Hz), 3.6 (CH$_3$CN)	−9.50	−78.5
12[b]	69	105–107, dec	3064, 2183 (C≡C), 2102 (CO), 1436, 1263, 1154, 1031	7.9–8.0 (24 H), 7.4–7.5 (36 H), 1.6 (6 H)	152.8 (CO, $^2J_{CP}$ = 7 Hz), 134.7 ($^2J_{CP}$ = 5 Hz), 131.8, 128.6 ($^3J_{CP}$ = 5 Hz), 127.1 ($^1J_{CP}$ = 30 Hz), 120.9 (OTf, $^1J_{CF}$ = 320 Hz), 119.8, 95.6 (β-C), 46.9 (α-C, $^2J_{CP}$ = 12 Hz), 3.0 (CH$_3$CN)	−12.29	−79.3

[a] CD_3CN NMR solution. [b] $CDCl_3$ NMR solution. [c] CCl_4 thin film. [d] Relative to tetramethylsilane internal standard. [e] Relative to 85% H_3PO_4 external standard. [f] Relative to $CFCl_3$ external standard. [g] **9b** is insufficiently soluble and not stable in solution to obtain a ^{13}C spectrum.

Scheme I



several hours in solution, but may be kept as a solid in a refrigerator. Reaction of **6** and **8** gave an impure oil as the product (~90% pure), which could not be isolated as a pure solid, whereas interaction of **11** with **8** gave only polymeric material. Products **9**, **10**, and **12** were characterized by multinuclear NMR and infrared spectroscopies. Specifically, the IR spectra clearly demonstrate a C≡O stretch at 2093–2102 cm^{-1} for **9**, **10**, and **12** and at 2122 cm^{-1} for **9b**, which is highly characteristic for hexacoordinated Ir(III) and Rh(III) species, respectively. Moreover, the IR data indicate the presence of the C≡C bond between 2124 and 2183 cm^{-1} and bands characteristic for the anionic triflate at 1263–1267 and 1031–1032 cm^{-1}. The presence of the OTf counterion was confirmed by the characteristic ^{19}F signal at −78 to −79 ppm. The existence of the mutually *trans* phosphines was indicated by the singlet at −9.85, −9.50, and −12.3 ppm for **9a**, **10**, and **12**, respectively, and the Rh-coupled doublet at 19.7 ppm for **9b** in the ^{31}P NMR spectrum. Further structural proof was provided by the ^{1}H and ^{13}C spectra that are completely consistent with the proposed structures. Particularly useful is the α-acetylenic carbon signal at 47–56 ppm with a carbon–phosphorus coupling of 12 Hz and the β signal at 96–109 ppm in the ^{13}C NMR spectra of **9a**, **10**, and **12**.

In conclusion, we have discovered a new way of preparing rigid-rod-like, cationic, bimetallic, σ-diyne complexes in a high-yield, single-step reaction using appropriate bisiodonium diyne ditriflate precursors.[10,11] This method corresponds to an alkynylation reaction using the organometallic species as a nucleophile and the alkynyliodonium salt as the alkynylating agent and represents a reversal of the traditional acetylide, RC≡C$^-$, chemistry. The use of other organometallic nucleophiles as well as other polyalkynyliodonium species is under active investigation and will be the subject of future reports.

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C_{60} as a Radical Sponge

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Facile additions of alkyl radicals and hydrogen atoms to C_{60} are observed to occur in a mass spectrometer ion source. These reactions have not been reported previously even though mass spectrometry played an important role in the discovery of the novel C_{60} allotrope of carbon[1,2], and numerous mass spectrometric studies have since been reported for the various fullerenes,[3-20] including

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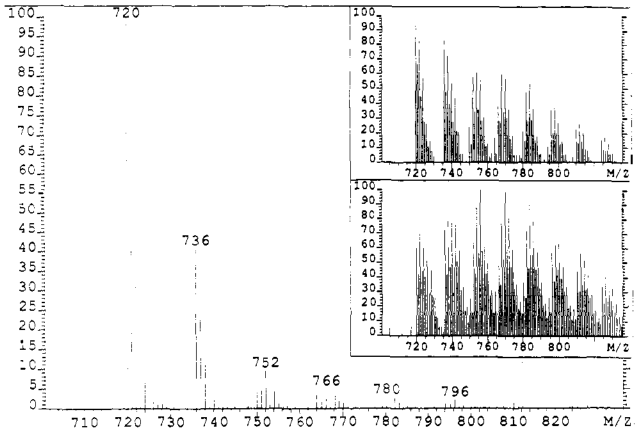
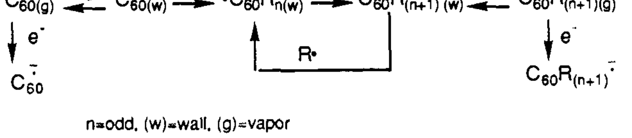


Figure 1. Electron-attachment mass spectrum of C_{60} using methane gas. C_{60} was introduced directly into the source (220 °C) through the heated (ca. 300 °C) solid probe. The insets show the spectra obtained after vaporizing C_{60} onto the walls of the source (<200 °C) and waiting several minutes before ramping the source temperature to 250 °C to vaporize the C_{60} products that were adsorbed on the walls.

Scheme I



chemical-ionization (CI)[3,4] and electron-attachement (EA)[5] studies in which adduct ions were observed.

Radical reactivity of C_{60} in solution has recently been reported in electron spin resonance studies.[21,22] In these studies, benzyl radical addition to C_{60} in toluene was observed by ESR spectroscopy and confirmed by fast atom bombardment (FAB) mass spectrometry. C_{60} bearing up to at least 15 benzyl groups was observed in the FAB mass spectrum. Similarly, up to 34 methyl groups were shown by FAB mass spectrometry to be attached to C_{60} in a solution in which methyl radicals were photochemically generated.[22] Alkylation of C_{60} with methyl iodide has also been demonstrated.[23] Addition of up to 24 methyl groups with a predominance of even numbers of methyl additions as determined by field ionization mass spectrometry was reported.[23]

Table I. Accurate Mass Determination of C_{60}, C_{70}, and Several of the Radical Products from a Single Mass Spectrum Acquired at 2000 Resolution (10% Valley) Using Poly(perfluoroisopropylene glycol) as an Internal Reference Mass Standard

measd *m/z*	elemental[a] composition	ppm error	calcd mass
719.9970	C_{60}	−4.2	720.0000
722.0093	$C_{60}H_2$	8.8	722.0157
736.0288	$C_{60}CH_4$	−3.4	736.0313
750.0385	$C_{60}C_2H_6$	−11.3	750.0469
752.0571	$C_{60}C_2H_8$	−7.3	752.0626
754.0765	$C_{60}C_2H_{10}$	2.3	754.0783
764.0628	$C_{60}C_3H_8$	0.3	764.0626
766.0818	$C_{60}C_3H_{10}$	−4.6	766.0783
768.0930	$C_{60}C_3H_{12}$	1.2	768.0939
778.0722	$C_{60}C_4H_{10}$	7.8	778.0782
839.9973	C_{70}	−3.2	840.0000

[a] Except for the low-mass ion in each cluster (e.g., 720, see Figure 1), ^{13}C isotopes are not resolved and contribute to the measured mass.

On the basis of the mass spectrometric characterization of the radical products from the solution work by Krusic et al.[21,22] and the discovery in this laboratory of compounds that efficiently trap radicals under CI conditions,[24] we looked for radical additions to C_{60} occurring in the CI ion source of a VG 70SE mass spectrometer. Figure 1 shows the EA mass spectrum obtained by vaporizing chromatographically purified C_{60} directly into a hot (220 °C) CI ion source using methane at ca. 65 Pa as the reagent gas. Under these conditions, methane acts to produce thermal electrons for ionization as well as positive reagent ions and neutral radicals.[24] The radicals produced in the CI source have been shown to react with only a few compounds such as tetracyanoquinodimethane (TCNQ), tetracyanoethylene, and pentacene.[25] The most abundant radicals trapped in the methane plasma are $^{\bullet}H$, $^{\bullet}CH_3$, and $^{\bullet}C_2H_5$.

With the exception of small impurities in the C_{60} sample (C_{62}, C_{64}, etc.), all of the ions higher in mass than the C_{60} molecular ion cluster in Figure 1 are not present in the EA (N_2) spectrum obtained after baking the source at 350 °C overnight. Accurate mass determinations of the ions appearing in the EA (CH_4) spectrum of C_{60} are displayed in Table I and show effective addition of H_2, CH_4, C_2H_6, C_2H_8, etc. On the basis of arguments presented in previous radical trapping studies,[24] these ions are interpreted to be produced by the mechanism shown in Scheme I. Thus, $C_{61}H_4$ would represent addition of $^{\bullet}CH_3$ and $^{\bullet}H$ to C_{60}; $C_{62}H_6$, addition of $^{\bullet}CH_3$ and $^{\bullet}CH_3$ and/or $^{\bullet}C_2H_5$ and $^{\bullet}H$; $C_{63}H_8$, addition of $^{\bullet}C_2H_5$ and $^{\bullet}CH_3$ and/or $^{\bullet}H$ and $^{\bullet}C_3H_7$, etc.

Further evidence that a radical reaction is involved was obtained by using TCNQ to trap the radicals produced in a CI nitrogen gas plasma containing a high partial pressure of 3-heptanone. The products of the TCNQ radical trapping reaction as determined from the EA mass spectra were compared to the C_{60} addition products observed under identical ion source conditions. The carbon-centered radicals trapped in both reactions were predominantly $^{\bullet}C_2H_5$, $^{\bullet}CH_3$, and $^{\bullet}C_4H_9$ in order of decreasing concentration.

An interesting feature of the mass spectrum shown in Figure 1 is the absence of ions at *m/z* 735. These ions would correspond to addition of $^{\bullet}CH_3$ to C_{60} with subsequent electron attachment. All ions of odd mass in the spectrum are either absent or of the expected intensity for the ^{13}C isotopes. This can be explained if the odd-electron C_{60} species cannot be ionized by electron capture, which seems unlikely, or if they adhere to the ion source walls. A mechanism can be envisioned in which odd-electron adducts bind tightly to the surface and are released upon formation of even-electron species. Further radical additions occurring before vaporization would continue the process and account for the multiple radical additions observed in Figure 1.

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The extent of alkyl addition to C_{60} is increased if the ion source is cooled slightly to reduce the rate of release of the condensed C_{60} species from the surface (Scheme I). The spectra shown in the insets of Figure 1 are obtained when the cooled ion source is heated after allowing several minutes for the products that are continuously being produced in a methane plasma to react with the condensed C_{60}. Ions were observed as high as m/z 834, which corresponds to $C_{67}H_{30}$, presumably from alkyl radical and hydrogen atom additions to C_{60}.

The facile reactivity of C_{60} with alkyl radicals suggests that caution should be used in interpreting mass spectra of fullerenes. Thus, an ion appearing 16 Da above the molecular ion of a fullerene could be $C_{60}O$ present in the sample or $C_{60}CH_4$ from reaction with radicals in the ion source. Accurate mass measurements are needed to distinguish these products.

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Charge-Transfer Emission in Meso-Linked Zinc Porphyrin-Anthraquinone Molecules

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We previously reported[1] the synthesis and characterization of a free-base porphyrin-anthraquinone molecule in which the quinone is attached at a meso position of tritolylporphyrin (I; see Chart I). The absorption spectra of I show perturbations in the bands of both the porphyrin and quinone groups that are independent of solvent polarity. The fluorescence spectra are only slightly red-shifted, but the lifetimes and intensities depend markedly on bulk dielectric constant (ϵ_s), with the major changes occurring over the range $4 < \epsilon_s < 9$.[1] The energetics for net electron transfer in I are not favorable, the sum of the redox potentials (in benzonitrile) being essentially isoenergetic with the porphyrin S_1 state. However, the short distance between the two moieties (~1.4 Å edge-to-edge) appears to compensate for the marginal energetics for electron transfer, depending on solvent polarity.

We have extended these studies to the Zn analogue (II), in which the energy gap between the S_1 state of the porphyrin and the sum of the redox potentials (measured in benzonitrile) is about −0.5 eV.[2] Thus, we had expected the onset of fluorescence quenching to occur at much lower solvent polarities than in the case of I. The absorption spectrum of II (Figure 1) displays the same kind of perturbations as I, with broadened and red-shifted porphyrin (P) bands along with a diminished quinone absorption (not shown). These perturbations depend on molecular structure (i.e., the position of the anthraquinone (AQ) substituent) but *not* on solvent polarity. The emission spectra, however, display a solvent-dependent band that is observed even in low-dipolar solvents such as benzene (Figure 2) and toluene. We assign this emission to a charge-transfer (CT) state, proof for which has been provided by time-resolved microwave conductivity measurements,[3] which reveal a transient dipole of ≥20 D with a lifetime of ~2 ns.

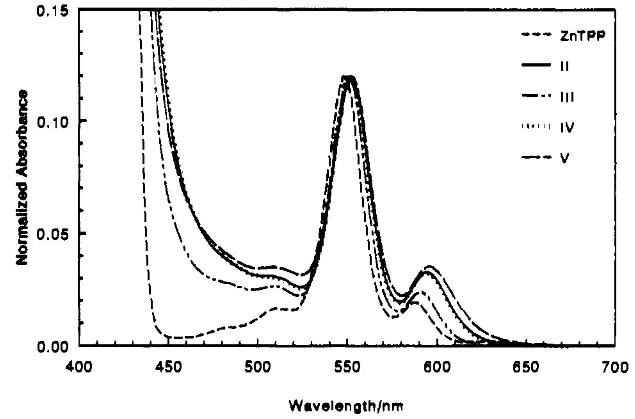
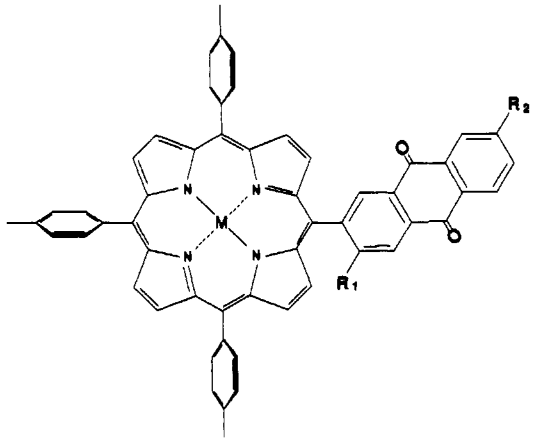


Figure 1. Absorption spectra of ZnTPP, II, III, IV, and V, all ~5 μM in benzene normalized at ~550 nm. The perturbations, relative to ZnTPP, depend strongly on the position of the AQ substituent (e.g., compare III with IV) but not on solvent dielectric constant. Note that the spectra of II and IV are virtually identical.

Chart I



Symbol	M	R_1	R_2
I	H_2	H	H
II	Zn	H	H
III	Zn	CH_3	H
IV	Zn	H	CH_3
V	Zn	H	Cl

Formation of CT states could involve twisting of the AQ moiety with respect to the plane of the porphyrin macrocycle.[5] To test this hypothesis, we synthesized a molecule (III) in which this kind of geometric flexibility is inhibited. As judged from the comparative spectral profiles, CT interactions in III appear to be greatly diminished relative to those in II (Figure 2).

In addition to inhibiting rotation about the P-AQ bond, the 3′-methyl group in III also reduces the driving force for CT formation by ~70 meV.[2] Thus, the relevant comparison of spectroscopic properties is between III and IV, which have nearly the same redox potentials, but the 7′-methyl group in the latter does not directly affect the P-AQ dihedral angle. In all solvents studied, the emission spectra of II and IV are quite similar to each other, but the spectra of III more closely resemble those of the

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[†] Formerly the Solar Energy Research Institute, operated for the U.S. Department of Energy by the Midwest Research Institute.

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