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Synthesis, Electrochemical Characterization, and Linear Free Energy Relationship of 1,3-Diphenyl-6-alkyl/arylfulvenes

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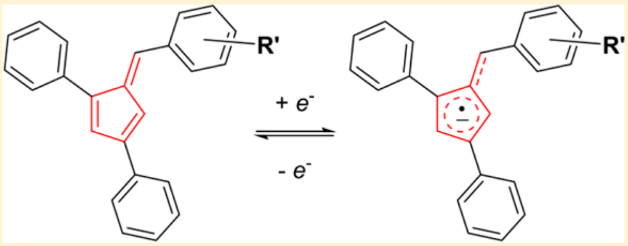
Supporting Information

ABSTRACT: A series of 1,3-diphenyl-6-alkyl/arylfulvenes was prepared, and the electrochemical properties were investigated. The addition of phenyl groups about the fulvene raised the reduction potential and helped to stabilize the electrochemically generated radical anion. The addition of various functional groups onto the phenyl ring at the 6-position of 1,3,6-triphenylfulvene results in a linear free energy relationship between reduction potential and the Hammett substituent constant, σ. Further extending the conjugation at the 6-position of 1,3-diphenyl-6-arylfulvenes increases the reversibility of the redox reactions, but does not appear to further stabilize the generated radical anion. This in-depth investigation provides evidence that the compounds studied may have utility in light-harvesting applications.



INTRODUCTION

Light-harvesting materials capture photons from sunlight and convert them into electrical energy when used in a photovoltaic cell. Even though sunlight is a naturally occurring and readily available resource, solar energy currently provides only a small fraction of the United States' energy needs. The biggest barriers toward wide-scale usage of photovoltaic cells are high cost and complex processability. Traditional photovoltaic cells fabricated from refined, crystalline silicon are too expensive to compete with energy produced from fossil fuels. As such, there has been a push to move toward more cost-effective "plastic" photovoltaic cells to allow for more widespread adoption.[1−4]

A lot of attention for organic light-harvesting materials has been given to polythiophene, poly(3,4-ethylenedioxythiophene), and corresponding derivatives modified with solubilizing groups.[5,6] Recently, however, several reports have theorized that the incorporation of fulvenes into polymers would result in low-bandgap materials suitable for polymer-based bulk heterojunction solar cells.[7,8] Unsubstituted fulvene is the nonaromatic carbon analogue of thiophene (Figure 1), and various small molecule derivatives have been shown to have tunable photophysical properties.[9−16]

While there have been multiple accounts regarding the photophysical properties of fulvenes, surprisingly little work has been done on the electrochemical nature of fulvenes. In 1946, the first report on the redox properties of fulvenes came from Wawzonek and Fan in their work on the reduction of unsaturated hydrocarbons.[17] By comparing 6,6-dimethylfulvene and 6,6-diphenylfulvene, they noticed that the addition of phenyl rings raised the reduction potential by ca. 0.3 V. Tacke et al. later commented that the addition of aromatic rings was needed to stabilize the electrochemically generated radical anion.[18] Without aromatic groups to stabilize the radical anion, the fulvenes were electrochemically irreversible and underwent undesired side reactions, such as hydrogen abstraction and oligomerization. Their attempts at electrochemically dimerizing fulvenes were largely unsuccessful as the increased steric bulk which stabilized the radical anion also prevents formation of *ansa*-ligands. The unpredictable reactivity of fulvenes and the ease at which unsubstituted fulvenes dimerize via Diels−Alder cycloaddition[19−22] has likely contributed to the low frequency of electrochemical fulvene research.

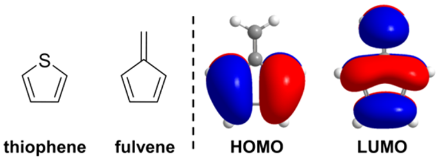


Figure 1. Left: Heterocyclic thiophene and nonaromatic fulvene comparison. Right: HOMO and LUMO of fulvene.

Aqad et al. studied the effects of donor and acceptor moieties on fulvenes and found that strong electron-withdrawing groups on the ring results in a positive shift in the reduction potential.[10] While they studied more than a dozen compounds, only those that had multiple methyl ester groups were found to have electrochemically reversible reductions. Most importantly was

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their finding that fulvenes are highly sensitive to various functional groups substituted on the ring portion of the molecule, and they theorized that fulvenes could prove to be an important class of tunable dyes. However, as far as the authors can tell, there has been no reported literature that looks at the effects of various substituents at the 6-position on the electronic nature of fulvenes.

Somewhat recently, Andrew et al. have shown that the incorporation of cyano-groups on the 6-position of fulvenes allows the molecules to undergo two consecutive, reversible, one-electron reductions.[12] They also showed that the fulvenes must be somewhat sterically hindered at the 1,4-positions to prevent dimerization, and an increase in conjugation about the ring raised the reduction potential of 6,6-dicyanofulvenes. Finke et al. also investigated the electronic properties of 6,6-dicyanofulvenes and found that the substituents on the ring determined whether the chemically generated radical anion was delocalized on the exocyclic position or around the substituted ring.[14]

The most recent report on the electrochemistry of fulvenes has been our recent publication on the incorporation of intact 1,3-diphenylfulvene units onto a polynorbornene backbone.[23] Encouraged by this and our work on the tunable photophysical properties of 1,3-diphenyl-6-alkyl/arylfulvenes,[15,16] we sought to further investigate the tunable ability of these compounds by varying key structural components and correlating the corresponding electrochemical response. In this work, we discuss how cyclic voltammetry (CV) and computational methods were used to investigate the properties of a series of alkyl- and aryl-substituted fulvenes. To the best of the authors' knowledge, this is the first comprehensive study on the electrochemical properties of substituted fulvenes, and this report provides further evidence for the viability of using this class of compounds in potential light-harvesting applications.

■ RESULTS AND DISCUSSION

Electrochemical Comparison of Alkyl- and Aryl-Substituted Fulvenes. CV was used to observe the differences in reduction potential in a series of alkyl- and aryl-substituted fulvenes. Figure 2 compares the voltammograms of compounds 1,3,6-tri(*tert*-butyl)fulvene (**1**), 1,3-diphenyl-6-(*tert*-butyl)-fulvene (**2**), and 1,3,6-triphenylfulvene (**3**) and shows the shifts in potential that arise from the addition of phenyl groups onto the core fulvene structure. Substituting the 1,3-*tert*-butyl groups on the ring for phenyl rings raises the reduction potential (E_{pc}) from −2.42 V for **1** to −1.99 for **2** and greatly increases the current response. The irreversible reduction seen in the voltammogram of **1** is likely due to dimerization, oligomer formation, or hydrogen abstraction by the generated radical anion. While the reduction of **1** is electrochemically irreversible, the addition of phenyl groups around the ring appears to help stabilize the generated radical anion, as evidenced by the small oxidation at −0.42 V. Comparing the anodic charge (Q_a) to the cathodic charge (Q_c)—calculated from the area under the curve—for **2** shows that only 13% of the charge is returned upon cycling. This indicates that the redox couple is only quasi-reversible and, when coupled with the large potential difference ca. 1.6 V, suggests slow electron transfer kinetics, likely a result of the pseudoaromatic nature of the reduced fulvene (Scheme 1).

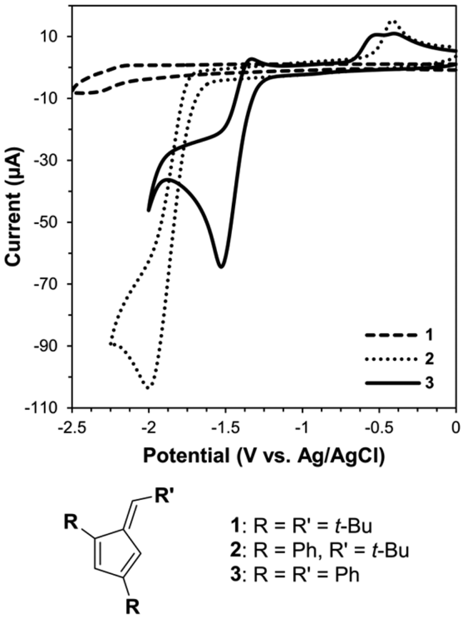
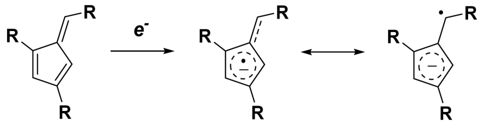


Figure 2. Representative CVs of 1,3,6-tri(*tert*-butyl)fulvene (**1**), 1,3-diphenyl-6-(*tert*-butyl)fulvene (**2**), and 1,3,6-triphenylfulvene (**3**). Five mM in 100 mM $NBu_4 \cdot PF_6$ (CH_2Cl_2), T = 25 °C, and ν = 100 mV/s.

Scheme 1. Single Electron Reduction of 1,3,6-Substituted Fulvenes and Major Resonance Contributor



The single electron reduction of fulvenes—either though chemical or electrochemical means—results in the generation of a radical anion, as shown in Scheme 1. Based on the ability of the fulvene radical anions to dimerize at the exocyclic position and form *ansa*-ligands,[24] the most stable resonance contributor depicts the radical localized on the exocyclic carbon and an aromatic anion centered about the cyclopentadienyl ring. The reduction of both **1** and **2** would result in a pseudoaromatic species, but the increased conjugation of **2** allows for resonance stabilization of the resulting radical anion, as evidenced by the positive shift in reduction potential and the quasi-reversible redox couple.

The addition of a third phenyl group at the 6-position of the fulvene (**3**) further raises E_{pc} to −1.55 V by stabilizing the generated exocyclic radical. The shift in potential from the addition of aromatics at the 6-position is consistent with previous work on fulvenes substituted solely at the 6-position,[17,18] and while Tacke et al. described reversible redox couples for phenyl-substituted fulvenes, neither voltammograms nor peak current data were reported. In addition to raising E_{pc}, the increased conjugation adds an oxidation peak at −1.35 V and overlapping peaks at −0.53 and −0.42 V. The new oxidation peaks indicate an increase in electrochemical reversibility and a more stabilized radical anion. The ratio of Q_a to Q_c for **3** shows a 55% charge return, indicating an increase in reversibility with increased conjugation; however, **3** is still only quasi-reversible and exhibiting nonideal Nernstian redox behavior.[32]

The scan rate (ν) was varied to further probe the electronic behavior of **3**. As seen in Figure 3, increasing ν from 0.025 to 0.600 V/s led to a gradual decrease in reduction potential of ca. 0.15 V, which is typical behavior for a quasi-reversible system where the equilibrium at the electrode's surface is not rapidly established.[32,33] Plotting i_{pc} against the square root of ν (Figure

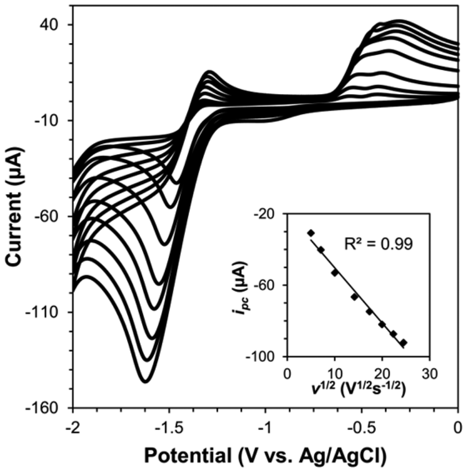


Figure 3. Representative CVs for 1,3,6-triphenylfulvene (**3**) with increasing scan rate: 0.025−0.600 V/s. Inset: plot of peak cathodic current (i_{pc}) vs square root of the scan rate ($v^{1/2}$). Five mM in 100 mM $NBu_4 \cdot PF_6$ (CH_2Cl_2) and T = 25 °C.

3, inset) resulted in a linear correlation, indicating a diffusion controlled system.

The exocyclic double bond of **3** was selectively hydrogenated in two steps via hydride delivery and protonation (Figure 4) to investigate its structural role on the electrochemical response of the fulvene. Hydrogenation of **3** to 1,3-diphenyl-5-benzylcyclopentadiene (**4**) resulted in a physical change from a dark red solid to a viscous yellow oil, a convenient visual confirmation that the exocyclic double bond had been compromised. Upon spectroscopic characterization of **4**, the distinct reduction peak at −1.55 V and the corresponding oxidation peaks for **3** are no longer present in the CV (Figure 4), demonstrating the importance of the fulvene core structure in organic electrochemistry.

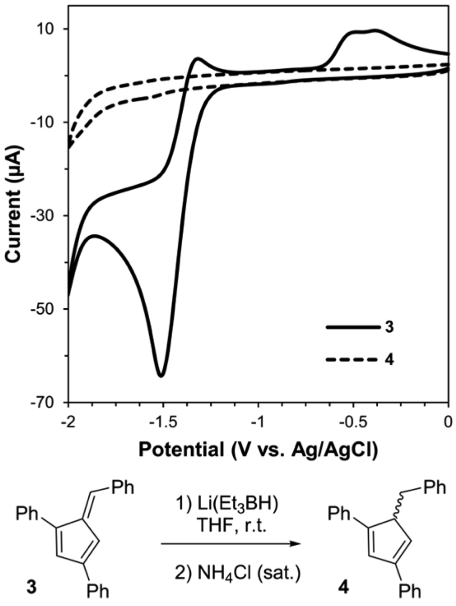


Figure 4. Representative CVs for 1,3,6-triphenylfulvene (**3**) and 1,3-diphenyl-5-benzylcyclopentadiene (**4**) and synthetic scheme for the selective hydrogenation of 3 to 4. Five mM in 100 mM $NBu_4 \cdot PF_6$ (CH_2Cl_2), T = 25 °C, and v = 100 mV/s.

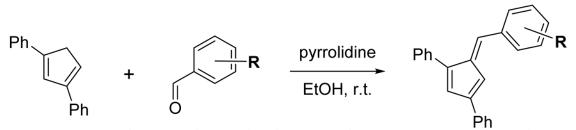
Substituent Effects on Reduction Potential. Tacke et al. noticed a negative shift in potential of 6-substituted fulvenes upon switching from phenyl to tolyl and mesityl groups.[18] Our group has also previously shown that interchanging substituents on 1,3,6-triphenylfulvene (**3**) is a facile method for tuning the photophysical properties of 1,3,6-triarylfulvenes.[15] As such, we sought to undertake a systematic study on the effects that various electron-donating and -withdrawing substituents on the 6-phenyl group of **3** would have on E_{pc}. Chart 1 lists the corresponding reduction potentials and electron affinities (EAs) for fulvenes **5**−**20** that were synthesized using the method of Stone and Little:[34] a pyrrolidine promoted condensation reaction between 1,3-diphenylcyclopentadiene and the corresponding benzaldehyde. Trimethylammonium iodide salt, fulvene **21**, was obtained by the room-temperature methylation of **5** from neat methyl iodide.

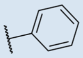
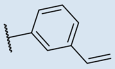
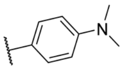
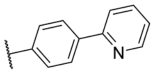
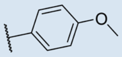
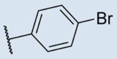
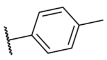
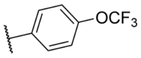
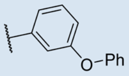
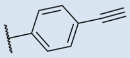
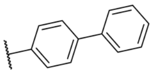
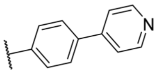
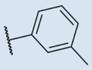
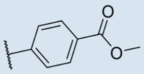
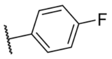
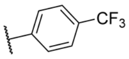
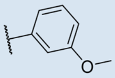
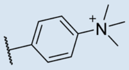
As expected, the reduction potentials of the 1,3-diphenyl-6-arylfulvenes substituted with electron-donating groups were lower than for those with electron-withdrawing groups. The electrostatic potential (ESP) maps shown in Figure 5 display how various substituents result in changes in electron density on 1,3-diphenyl-6-arylfulvenes. Unsubstituted compound **3** has the majority of the electron density dispersed about the fulvene ring and the phenyl groups at the 1- and 3-positions. The addition of a strong electron-donating dimethylamino substituent *para* to the fulvene (**5**) focuses the electron density on the ring of the fulvene. This makes the injection of an electron into the system less favorable and is reflected in the lowering of E_{pc} from −1.55 to −1.82 V. There is almost no change in the ESP map for a weak electron-donating *para*-methyl group (**7**) when compared to **3**, which correlates well with the small decrease in E_{pc} to −1.60 V. The ESP maps for the electron-withdrawing *para*-methyl ester (**19**) and *para*-trifluoromethyl (**20**) substituted fulvenes show similar removal of electron density from the fulvene core, and the reduction potentials are very close at −1.34 and −1.32 V, respectively. Despite the fact that **19** would resonance stabilize the generated radical anion, whereas **20** is solely removing electron density through inductive effects, indicates that both resonance and inductive contributions have a strong effect on the reduction potentials of the analyzed fulvenes. The largest calculated change in electron density was for the *para*-trimethylammonium substituted fulvene (**21**). Having a distinct cation on the fulvene, rather than electronegative atoms or resonance contributors, significantly reduces the electron density on the fulvene core. The greatly decreased electron density makes the electrochemical reduction more thermodynamically favorable, and this is reflected in the increased reduction potential of −1.03 V for **21**.

The EAs of 1,3-diphenyl-6-arylfulvenes were estimated from the onset of reduction (via a straight-line approximation in the voltammogram) and corrected to an external Fc/Fc^+ redox couple (0.43 V vs Ag/AgCl) (Chart 1).[35−37] The EA values varied from 3.01 to 3.69 eV and followed roughly the same trend with regards to aromatic directing groups: higher values for strongly electron-withdrawing groups and lower values for strongly electron-donating groups. The 1,3-diphenyl-6-arylfulvenes EAs are comparable to 6,6-dicyanofulvenes[12] (ca. 3.9 eV) and phenyl−C_{61}−butyric acid methyl ester[2] (PCBM, 4.2 eV) and makes them interesting candidates for hole-transporting materials.

The effects of substituents altering electrochemical behavior are a well-known phenomenon,[38−41] and, as such, differences in

Chart 1. Synthesis, Reduction Potentials (E_{pc}), and Electron Affinities (EAs) of 1,3-Diphenyl-6-arylfulvenes



Entry	Substituent	E_{pc}[a] (V)	EA[b] (eV)	Entry	Substituent	E_{pc}[a] (V)	EA[b] (eV)
3		-1.55	3.21	**13**		-1.52	3.26
5		-1.82	3.01	**14**		-1.49	3.26
6		-1.63	3.14	**15**		-1.48	3.24
7		-1.61	3.18	**16**		-1.46	3.27
8		-1.57	3.18	**17**		-1.45	3.28
9		-1.56	3.20	**18**		-1.42	3.25
10		-1.56	3.19	**19**		-1.39	3.27
11		-1.54	3.21	**20**		-1.33	3.31
12		-1.53	3.20	**21**[c]		-1.03	3.69

[a] Five mM in 100 mM $NBu_4 \cdot PF_6$ (CH_2Cl_2), $T = 25$ °C, and $\nu = 100$ mV/s. [b] Calculated by the straight line approximation of the onset of reduction (E_{on}), relative to ferrocene (Fc), via equation: $EA = (E_{on} - E_{1/2(Fc)}) + 4.8$ eV [c] Synthesized from compound **5** and neat methyl iodide.

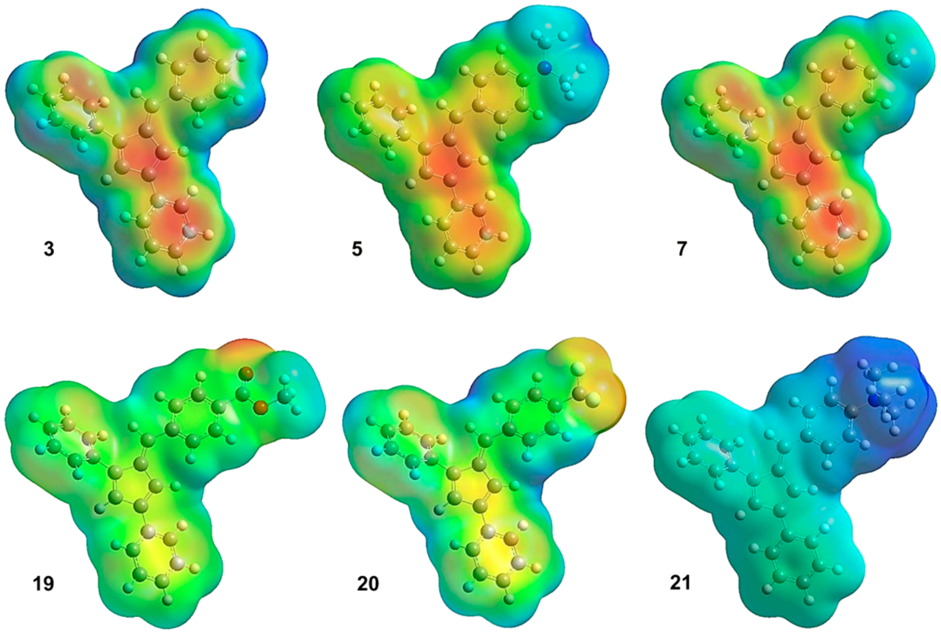


Figure 5. Electrostatic potential maps for 1,3,6-triphenylfulvene (**3**), 1,3-diphenyl-6-([4-(dimethylamino)phenyl)]fulvene (**5**), 1,3-diphenyl-6-(4-methylphenyl)fulvene (**7**), 1,3-diphenyl-6-([4-methyl benzoate)]fulvene (**19**), 1,3-diphenyl-6-([4-(trifluormethyl)phenyl)]fulvene (**20**), and 1,3-diphenyl-6-([4-(trimethylammonium)phenyl)]fulvene (**21**).

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E_{pc} for 1,3-diphenyl-6-arylfulvenes should correlate to the Hammett equation:[42]

$$\log \frac{K_X}{K_H} = \log K_X - \log K_H = \rho\sigma \tag{1}$$

In the traditional Hammett equation, K_X is the equilibrium constant for a reaction concerning substituted aryl species, K_H is the equilibrium constant for the unsubstituted parent compound, σ is the Hammett substituent constant, and ρ is the reaction sensitivity constant. In the case of electrochemical reactions,[43] the equilibrium constants are defined as

$$\log K = \left(\frac{nF}{2.303RT}\right)E^\circ \tag{2}$$

where n is the number of electrons, F is the Faraday constant, T is the temperature in Kelvin, R is the gas constant, and E° is the standard electrochemical potential. Substituting eq 2 into eq 1 yields eq 3, which can be simplified into eq 4:

$$\left(\frac{nF}{2.303RT}\right)E_X{}^\circ - \left(\frac{nF}{2.303RT}\right)E_H{}^\circ = \rho\sigma \tag{3}$$

$$\left(\frac{nF}{2.303RT}\right)\Delta E^\circ = \rho\sigma \tag{4}$$

Standard electrochemical potentials for a reversible redox couple are determined using the half-wave potential ($E_{1/2}$).[43,44] The fulvene reduction potentials listed in Chart 1 were quasi-reversible in nature, making an accurate calculation of $E_{1/2}$ unfeasible. However, since E_{pc} was measured using the same scan rate, working electrode, electrolyte concentration, and compound concentration and assuming the reduction rate is similar for each substituted fulvene, then eq 5:

$$\Delta E_{pc} = E_{pcX} - E_{pcH} \tag{5}$$

can be substituted into eq 4 to give eq 6.[41] Rearranging eq 6 and inputting values for all constants affords eq 7, which can be used to plot changes in E_{pc} due to substituent effects against the σ.

$$\left(\frac{nF}{2.303RT}\right)\Delta E_{pc} = \rho\sigma \tag{6}$$

$$\Delta E_{pc} = (0.0592\rho)\sigma \tag{7}$$

The values of ΔE_{pc} for the 1,3-diphenyl-6-arylfulvenes listed in Chart 1 were plotted against the corresponding Hammett substituent constants (Figure 6).[42] The free energy relationship for compounds **5**−**21** was roughly linear ($R^2 = 0.89$, $R = 0.94$) with a notable outlier for the trimethylammonium salt **21** (Figure 6, unfilled marker). Removing **21** from the Hammett plot increases the linear correlation significantly ($R^2 = 0.98$, $R = 0.99$), indicating that the distinct cation has a more significant inductive effect than simple differences in electronegativity. Based on the slope of the line and eq 7, the ρ value for compounds **5**−**20** was 5.73. The large, positive ρ value indicates a strong influence of the substituents on the reduction potential and a buildup of negative charge during the electrochemical reaction. The buildup of negative charge is expected since the electrochemical reduction of the fulvene, by definition, results in a discrete anion being generated.

Even though E_{pc} values for 1,3-diphenyl-6-arylfulvenes **5**−**21** had an adequate linear free energy correlation when plotted against σ, it is not beyond reason that $\sigma-$ might give a better correlation since the substituents on the 6-postion could resonance stabilize the electrochemically generated radical anion shown in Scheme 1. As shown in Figure 7, the linear free energy correlation was significantly worse when ΔE_{pc} values for **5**−**21** were plotted against $\sigma-$ ($R^2 = 0.59$, $R = 0.77$). The substituents with the most significant difference between σ and $\sigma-$ were the electron-rich p-NMe$_2$ fulvene, **5**, and the electron-poor p-NMe$_3$ derivative, **21** . Omitting these points from the $\sigma-$ free energy plot resulted in an increase in linearity ($R^2 = 0.84$, $R = 0.92$), but the correlation was still lower than for the σ plot. The poor correlation against $\sigma-$ suggests that the electrochemically generated anion is not being greatly stabilized by the substituents on the phenyl ring at the 6-position of the fulvene. Instead, the poor anion stabilization indicates a preference for localization of the anion about the cyclopentadienyl portion of the reduced fulvenes, likely due to the aromatic nature it would impart. Therefore, the linear free energy correlation for ΔE_{pc} values plotted against σ suggests the substituents are effecting the radical stabilization rather than anion stabilization. This also indicates localization of the electrochemically generated radical at the exocyclic carbon of the reduced fulvene rather than about the cyclopentadienyl ring.

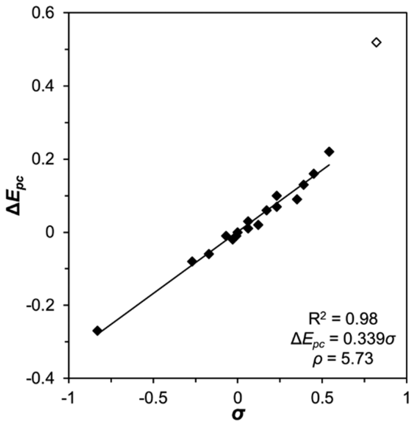

Figure 6. Plots of σ vs of ΔE_{pc} values for 1,3-diphenyl-6-arylfulvenes: **5**−**20** are filled, **21** is unfilled. All σ values are from ref 42.

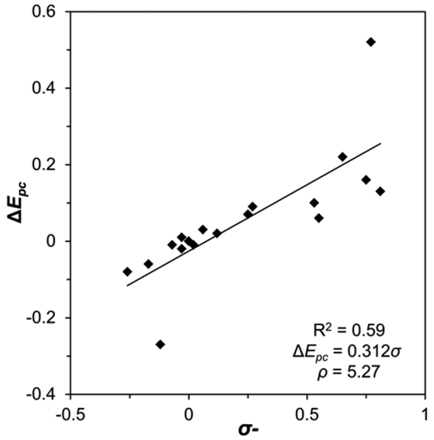

Figure 7. Plot of $\sigma-$ vs of ΔE_{pc} values for 1,3-diphenyl-6-arylfulvenes **5**−**21**. All $\sigma-$ values are from ref 42.

Effect of Extended Conjugation at the 6-Position of the Fulvene. Having demonstrated that a substituted phenyl ring at the 6-position of the fulvene can stabilize or destabilize the electrochemically generated radical, we sought to replace the

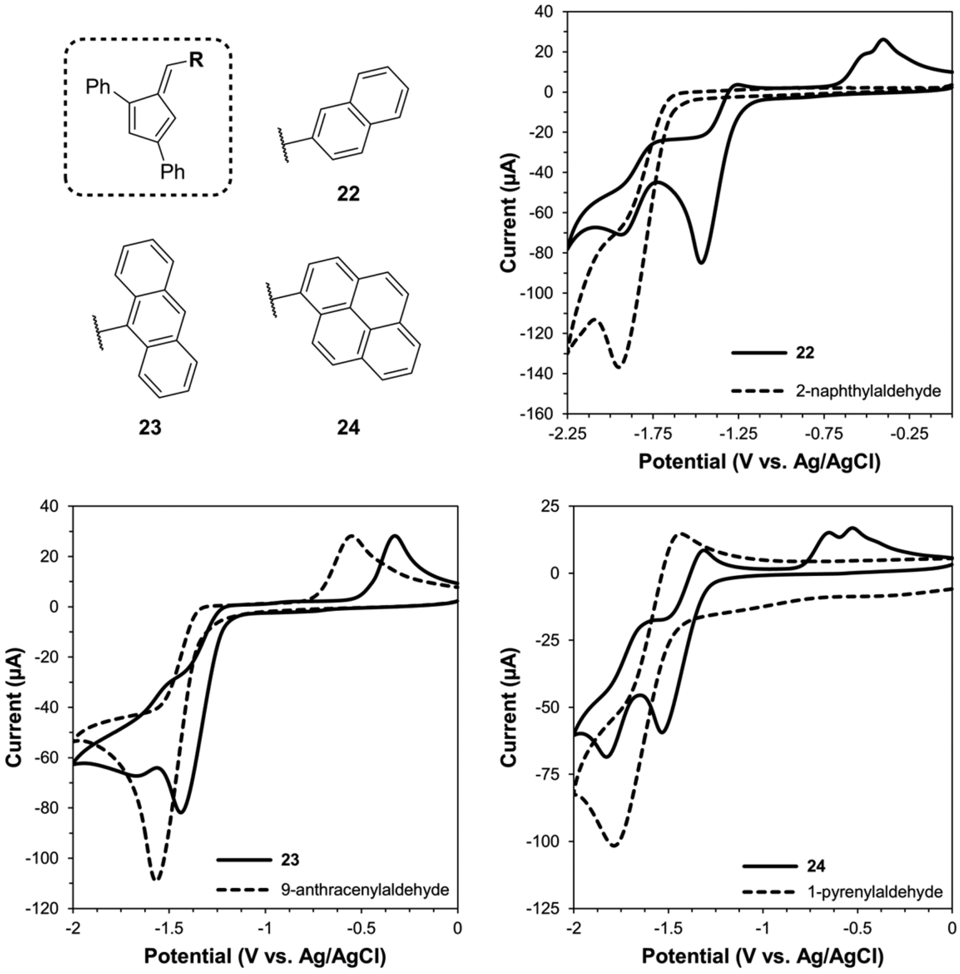

Figure 8. Representative CVs for 1,3-diphenyl-6-(2-naphthyl)fulvene (**24**), 1,3-diphenyl-6-(9-anthracenyl)fulvene (**25**), and 1,3-diphenyl-6-(1-pyrenyl)fulvene (**26**) and their corresponding aldehyde starting material. Five mM in 100 mM $NBu_4 \cdot PF_6$ (CH_2Cl_2), T = 25 °C, and ν = 100 mV/s.

phenyl ring with more complex aromatic groups and investigate the effect on the reduction potential. Extending the conjugation at the 6-position should, presumably, stabilize the generated radical anion and raise E_{pc} further. Figure 8 compares the cyclic voltammograms of 1,3-diphenyl-6-(2-naphthyl)fulvene (**22**), 1,3-diphenyl-6-(9-anthracenyl)fulvene (**23**), and 1,3-diphenyl-6-(1-pyrenyl)fulvene (**24**) with their corresponding aldehyde starting material. The addition of more complex aromatic groups onto the 6-position resulted in a second reduction peak in the voltammograms for **22**, **23**, and **24**. By comparing the voltammograms of the newly synthesized fulvenes with their corresponding aldehydes, it is possible to elucidate changes in the electrochemical behavior when compared to compound **3**. Compound **22** has two reduction peaks at −1.47 and −1.94 V, which, as seen by the reduction of 2-naphthaldehyde, corresponds to the reduction of the fulvene and subsequent reduction of the naphthyl group at the 6-position. The positive shift in E_{pc} for the fulvene reduction suggests further stabilization of the electrochemically generated radical anion. Compound **22** has a small oxidation peak at −1.26 V and overlapping oxidation peaks at −0.51 and −0.41 V. The Q_a/Q_c ratio shows that only 36% of the total charge is being returned upon potential cycling, but removing the irreversible naphthalene reduction at −1.94 V increases the charge return to 65%. The increased conjugation increases the electrochemical reversibility, but the redox couple is still quasi-reversible.

Compound **23** and 9-anthraldehyde have reduction peaks at −1.44 and −1.57 V, respectively, which likely centers the first reduction of **23** on the anthracenyl portion of the molecule rather than the fulvene. The positive shift in E_{pc} for **23** is likely due to a weak electron-withdrawing effect from the electron-poor fulvene. The second reduction for **23** at −1.66 V is that of the fulvene exocyclic double bond and is at a lower potential than **3** due to the additional electron density already centered on the 6-position from the reduction of the anthracene. There are two oxidations for **23**: a small shoulder at −1.49 and a larger peak at −0.32 V. The first oxidation likely correlates to similar peaks for **3** and **22**, and the larger peak is a combination of the fulvene and anthracene oxidations. Further increasing the conjugation at the 6-position again increases the reversibility, as seen by 77% charge return based on the Q_a/Q_c ratio.

A similar phenomenon occurs with the pyrene-substituted fulvene, **24**: the initial fulvene reduction occurs at −1.50 V, and the buildup of negative charge shifts the reduction of the pyrene substituent from −1.78, for the aldehyde, to −1.84 V. The addition of a more complex aromatic groups onto the 6-position of the fulvene only moderately increases E_{pc} for **24**, and the charge return increases to 80%.

■ CONCLUSIONS

Cyclic voltammetry provides a quick and facile method to characterize and screen electroactive species for usage in organic electronics. We have electrochemically characterized a series of 1,3,6-alkyl-/aryl-substituted fulvenes and shown that increases in conjugation about the fulvene core stabilize the generated radical anion. Selectively hydrogenating the exocyclic double bond of the fulvene negated the electrochemical behavior of these compounds, further demonstrating the need to stabilize this reactive site by extending the conjugation of the system. All 1,3-diphenyl-6-alkyl/arylfulvenes analyzed by CV were electrochemically quasi-reversible, but exhibited diffusion controlled redox behavior. Increasing the conjugation at the 6-position beyond a phenyl group resulted in only moderate increases in thermodynamic reduction favorability, as evidenced by the small increase in reduction potentials, but the degree of reversibility for the compounds was enhanced.

We have also demonstrated that the reduction potential of 1,3-diphenyl-6-arylfulvenes is strongly influenced by substituents at the 6-position and exhibits a linear free energy relationship when plotted against the Hammett constant σ. The linear correlation allows for prediction of reduction potentials of related fulvene molecules and may aid in the design of organic electronics based on these compounds. Efforts to incorporate 1,3-diphenyl-6-arylfulvenes into polymers for light-harvesting materials are ongoing.

■ EXPERIMENTAL SECTION

General Methods and Materials. Solvents, starting materials, and reagents were purchased from commercial sources as reagent grade or higher quality and used as received unless otherwise noted. HPLC-grade THF was dried and deoxygenated by passage through a solvent purification system equipped with Cu/Al columns. Compounds diphenylcyclopentadiene,[15] 1,3,6-tri(*tert*-butyl)fulvene (**1**),[25] 1,3-diphenyl-6-(*tert*-butyl)fulvene[15] (**2**), 1,3,6-triphenylfulvene[15] (**3**), 1,3-diphenyl-6-(3-phenoxyphenyl)fulvene[15] (**8**), 1,3-diphenyl-6-(3-vinylphenyl)fulvene[26] (**13**), 1,3-diphenyl-6-(4-trifluoromethylphenyl)-fulvene[15] (**20**), and 1,3-diphenyl-6-(1-pyrenyl)fulvene[15] (**24**) were synthesized according to previously reported procedures.

Instrumentation. All ^{1}H, ^{13}C, and ^{19}F NMR spectra were obtained under ambient conditions using a 400 MHz instrument, and chemical shifts were reported in parts per million (δ). Chemical shifts were referenced using the residual solvent peak $CDCl_3$ (^{1}H NMR: δ 7.26; ^{13}C NMR: δ 77.0). ^{19}F NMR was referenced to $CFCl_3$ (δ 0.00).

Elemental analysis (CHN) was performed using acetanilide as a standard. The combustion and reduction tubes were held at 1150 and 950 °C, respectively, and a stream of argon at 1100−1200 mbar was used as a carrier gas.

CV was performed with a potentiostat using a Ag/AgCl pseudoreference electrode, platinum wire counter electrode, and a 3 mm glassy carbon working electrode. All electrochemical experiments were performed at 5 mM in nitrogen sparged 100 mM tetrabutylammonium hexafluorophosphate (CH_2Cl_2) at 25 °C.

Melting points were determined using differential scanning calorimetry in a nitrogen environment sealed in aluminum hermetic pans with an empty sealed hermetic pan serving as the reference. Melt transitions were reported using graphical software on the first heat cycle at a rate of 5 °C/min.

Computational Methods. All calculations were performed using Gaussian 03 on a desktop personal computer.[27] The computational method used was the density functional theoretical method using Becke's 3-parameter exchange functional plus the correlation functional of Lee, Yang, and Parr (abbreviated B3LYP)[28,29] along with the standard Gaussian basis set labeled 6-311+G(d,p).[30] Minimum energy geometries were determined for all target molecules using standard options, and minima were visualized using the GaussView program.[31] Electrostatic potentials were calculated from the checkpoint files generated as part of the optimization calculations, using a medium grid. ESP values were mapped to an isosurface at a density value of 0.0004 e/Å.[3] Cartesian coordinates of the optimized geometries of six selected arylfulvenes and their total electronic energies are given in the Supporting Information.

Materials Synthesis. *1,3-Diphenyl-5-benzylcyclopentadiene (**4**).* To a flame-dried flask under N_2 were added **3** (0.261 g, 0.852 mmol) and THF (5 mL). Lithium triethylborohydride (1.27 mL, 1 M THF) was added to the reaction mixture dropwise via syringe. The solution rapidly faded from dark red to pale yellow. The color of the reaction mixture was exposed to air, and saturated ammonium chloride solution (4 mL) was added dropwise to quench the reaction. The organic phase was separated, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was extracted with hexanes, filtered through a plug of Celite, and purified via flash chromatography (90:10, hexanes:ethyl acetate) to yield viscous yellow oil **4** as a mixture of isomers (0.131 g, 50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.41 and 3.94 (2 s, 1H), 3.87 (s, 1H), 3.96 (s, 1H), 6.74 and 7.01 (s, 1H), 7.25−7.51 (m, 16H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 34.1, 34.9, 43.9, 44.2, 124.7, 124.9, 126.1, 126.5, 126.8, 127.6, 127.9, 128.5, 128.6, 128.7, 127.7, 128.8, 131.5, 135.8, 137.1, 140.1, 140.2, 140.5, 144.8. Anal. calcd for $C_{24}H_{20}$: C, 93.45; H, 6.54. Found: C, 93.40; H, 6.60.

*1,3-Diphenyl-6-[4-(dimethylamino)phenyl]fulvene (**5**).* To a stirred suspension of 1,3-diphenylcyclopentadiene (0.250 g, 1.15 mmol) and 4-(dimethylamino)benzaldehyde (0.171 g, 1.15 mmol) in absolute ethanol (5 mL) under N_2 was added pyrrolidine (144 μL, 1.73 mmol). The color of the reaction mixture gradually faded from pale yellow to dark orange. The reaction mixture was stirred at room temperature for 4 h and then placed in an ice bath. The resulting precipitate was vacuum filtered, washed with cold absolute ethanol, and vacuum-dried to afford a dark brownish-orange powder (0.36 g, 90%). Mp: 126−127 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.07 (s, 6H) 6.71−6.77 (m, 2H), 6.93 (d, 1H), 7.17 (d, 1H), 7.20 (s, 1H), 7.26−7.50 (overlapping m's, 8H), 7.61−7.65 (m, 2H), 7.70−7.75 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 40.2, 112.1, 114.3, 125.8, 126.0, 126.6, 127.3, 128.3, 128.6, 129.5, 133.0, 135.9, 136.9, 140.1, 140.8, 145.0. Anal. calcd for $C_{26}H_{23}N$: C, 89.36; H, 6.63; N, 4.01. Found: C, 89.55; H, 6.69; N, 3.76.

*1,3-Diphenyl-6-(4-methoxyphenyl)fulvene (**6**).* Employing a similar procedure outlined for **5**, 1,3-diphenylcyclopentadiene (0.510 g, 2.34 mmol), 4-anisaldehyde (326 μL, 2.69 mmol), and pyrrolidine (292 μL, 3.51 mmol) were used to obtain **6** as a dark red solid (0.700 g, 89%). Mp: 109−111 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.88 (s, 3H), 6.96−7.01 (m, 3H), 7.08 (m, 1H), 7.23 (s, 1H), 7.28−7.50 (overlapping m's, 8H), 7.61−7.65 (m, 2H), 7.70−7.74 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 114.3, 126.0 127.0 127.2, 127.9, 128.4, 128.6, 129.5, 129.9, 132.5, 125.5, 136.1, 138.7, 141.8, 142.3, 146.2, 160.8. Anal. calcd for $C_{25}H_{20}O$: C, 89.25; H, 5.99. Found: C, 89.03; H, 6.04.

*1,3-Diphenyl-6-(4-methylphenyl)fulvene (**7**).* To a vigorously stirred mixture of 1,3-diphenylcyclopentadiene (2.03 g, 9.30 mmol) in absolute ethanol (50 mL) under N_2 were added *p*-tolualdehyde (1.33 g, 11.1 mmol) and pyrrolidine (1.20 mL, 14.3 mmol). The color of the reaction mixture gradually faded from pale yellow to brick red. The reaction mixture was maintained at room temperature for 18 h. The resulting precipitate was vacuum filtered, washed with cold absolute ethanol, and vacuum-dried to afford a dark red powder (2.68 g, 90%). Mp: 133−134 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 7.00 (d, 1H), 7.08 (m, 1H), 7.27−7.52 (overlapping m's, 11H), 7.54−7.59 (m, 2H), 7.70−7.75 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4,114.8, 126.1, 127.1, 127.7, 127.9, 128.4, 128.6, 129.4, 129.5, 130.9, 134.2, 135.3, 136.1, 138.8, 139.7, 141.8, 143.5, 146.5. Anal. calcd for $C_{25}H_{20}$: C, 93.71; H, 6.29. Found: C, 93.77; H, 6.23.

*1,3-Diphenyl-6-(4-biphenyl)fulvene (**9**).* Employing a similar procedure outlined for **7**, 1,3-diphenylcyclopentadiene (1.67 g, 7.65 mmol), biphenyl-4-carboxaldehyde (1.57 g, 8.62 mmol), and pyrrolidine (1001 μL, 11.99 mmol) were used to obtain **9** as a dark red solid (2.85 g, 97%). Mp: 160−162 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.77 (s, 1H), 7.13−7.18 (m, 2H), 7.19−7.24 (m, 3H) 7.28−7.44 (overlapping m's, 15H), 7.51−7.57 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 114.5, 126.1, 127.2, 127.4, 127.9, 128.1, 128.5, 128.8, 129.0, 129.5, 131.2, 135.1, 136.0, 138.0, 140.2, 141.8, 141.9, 144.1, 146.9. Anal. calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.38; H, 5.62.

*1,3-Diphenyl-6-(3-methylphenyl)fulvene (**10**).* To a vigorously stirred mixture of 1,3-diphenylcyclopentadiene (0.513 g, 2.35 mmol) in absolute ethanol (5 mL) under N_2 were added freshly distilled *m*-tolualdehyde (291 μL, 2.47 mmol) and pyrrolidine (294 μL, 3.53 mmol). The color of the reaction mixture gradually faded from pale yellow to brick red. The reaction mixture was maintained at room temperature for 18 h. The resulting precipitate was vacuum filtered, washed with cold absolute ethanol, and vacuum-dried to afford a sticky, dark red solid. The crude product was extracted with hexanes, washed with dilute HCl, dried with MgSO4, and filtered. The solvent was removed under reduced pressure to yield **10** as a dark red solid (0.326 g, 43%). Mp: 100−101 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 7.01 (d, 1H), 7.03 (m, 1H), 7.17−7.61 (overlapping m's, 13H), 7.6−7.74 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.8, 114.8, 126.2, 127.1, 127.8, 127.9, 128.4, 128.8, 129.5, 129.9, 131.5, 135.1, 136.1, 137.0, 138.4, 138.9, 141.8, 144.2, 146.8. Anal. calcd for $C_{25}H_{20}$: C, 93.71; H, 6.29. Found: C, 93.46; H, 6.48.

*1,3-Diphenyl-6-(4-fluorophenyl)fulvene (**11**).* Employing a similar procedure outlined for **7**, 1,3-diphenylcyclopentadiene (0.505 g, 2.31 mmol), 4-fluorobenzaldehyde (301 μL, 2.81 mmol), and pyrrolidine (290 μL, 3.47 mmol) were used to obtain **11** as a dark red powder (0.622 g, 83%). Mp: 97−99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.96−7.03 (m, 2H), 7.11−7.18 (m, 2H), 7.22 (s, 1H), 7.28−7.52 (overlapping m's, 8H), 7.59−7.66 (m, 2H), 7.68−7.72 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 113.9, 115.8, 116.1, 126.1, 127.0, 128.1, 128.4, 128.8, 129.4, 132.5, 135.2, 136.0, 137.3, 141.8, 144.0, 146.9, 164.5. ^{19}F NMR (376 MHz) δ −111.2. Anal. calcd for $C_{24}H_{17}F$: C, 88.86; H, 5.28. Found: C, 88.57; H, 5.38.

*1,3-Diphenyl-6-(3-methoxyphenyl)fulvene (**12**).* Employing a similar procedure outlined for **5**, 1,3-diphenylcyclopentadiene (0.500 g, 2.29 mmol), 3-anisaldehyde (0.320 mL, 2.63 mmol), and pyrrolidine (286 μL, 3.44 mmol) were used to obtain **12** as a dark red solid (0.618 g, 80%). Mp: 166−118 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.87 (s, 3H), 6.93−6.97 (br dd, 1H), 7.01 (d, 1H), 7.06 (m, 1H), 7.15 (t, 1H), 7.23−7.51 (overlapping m's, 11H), 7.69−7.73 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.2, 114.7, 115.2, 115.9, 123.4, 126.3, 127.3, 128.2, 128.6, 128.9, 129.6, 129.9, 135.4, 136.2, 138.6, 141.9, 144.7, 147.0, 160.0. Anal. calcd for $C_{25}H_{20}O$: C, 89.25; H, 5.99. Found: C, 89.68; H, 5.97.

*1,3-Diphenyl-6-[4-(2-pyridyl)phenyl]fulvene (**14**).* Employing a similar procedure outlined for **7**, 1,3-diphenylcyclopentadiene (2.00 g, 9.16 mmol), 4-(2-pyridyl)benzaldehyde (2.01 g, 11.0 mmol), and pyrrolidine (1191 μL, 14.27 mmol) were used to obtain **14** as a maroon powder (2.48 g, 73%). Mp: 141−143 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.01 (d, 1H), 7.09 (m, 1H), 7.24−7.52 (overlapping m's, 10H), 7.69−7.83 (overlapping m's, 6H), 8.08−8.12 (m, 2H), 8.73 (dt, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 114.5, 120.5, 122.5, 126.1, 127.0, 127.1, 128.0, 128.1, 128.5, 128.7, 129.3, 131.2, 135.1, 136.0, 136.9, 137.7, 137.9, 139.8, 141.6, 144.7, 146.9, 149.9, 156.3. Anal. calcd for $C_{29}H_{21}N$: C, 90.83; H, 5.52; N, 3.65. Found: C, 91.06; H, 5.52; N, 3.42.

*1,3-Diphenyl-6-(4-bromophenyl)fulvene (**15**).* Employing a similar procedure outlined for **7**, 1,3-diphenylcyclopentadiene (5.00 g, 22.9 mmol), 4-bromobenzaldehyde (5.10 g, 27.56 mmol), and pyrrolidine (2817 μL, 33.75 mmol) were used to obtain **15** as a dark red powder (8.21 g, 93%). Mp: 146−147 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.97 (m, 1H), 7.01 (d, 1H), 7.17 (s, 1H), 7.28−7.53 (overlapping m's, 10H), 7.55−7.61 (m, 2H), 7.68−7.73 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 114.1, 123.7, 124.9, 126.2, 126.9, 127.2, 128.2, 128.4, 128.5, 128.8, 128.9 129.4, 132.0, 132.1, 135.0, 135.8, 136.0, 136.9, 141.8, 144.9, 147.2. Anal. calcd for $C_{24}H_{17}Br$: C, 74.81; H, 4.45. Found: C, 75.16; H, 4.44.

*1,3-Diphenyl-6-(4-trifluoromethoxyphenyl)fulvene (**16**).* Employing a similar procedure outlined for **7**, 1,3-diphenylcyclopentadiene (0.503 g, 2.30 mmol), 4-trifluormethoxybenzaldehyde (362 μL, 2.53 mmol), and pyrrolidine (289 μL, 3.46 mmol) were used to obtain **16** as a maroon powder (0.700 g, 78%). Mp: 109−110 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.97 (m, 1H), 7.01 (d, 1H), 7.22 (s, 1H), 7.27−7.50 (overlapping m's, 10H), 7.63−7.68 (m, 2H), 7.69−7.74 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 114.0, 120.0 (q, $^1J_{C-F}$ = 257 Hz), 121.1, 126.1, 127.1, 128.1, 128.5, 128.6, 128.8, 129.4, 132.0, 135.0, 135.6, 135.7, 136.2, 141.8, 145.0, 147.3. ^{19}F NMR (376 MHz) δ −57.7. Anal. calcd for $C_{25}H_{17}OF_3$: C, 76.91; H, 4.39. Found: C, 76.85; H, 4.24.

*1,3-Diphenyl-6-(4-ethynylphenyl)fulvene (**17**).* Employing a similar procedure outlined for **7**, 1,3-diphenylcyclopentadiene (1.00 g, 4.58 mmol), 4-ethynylbenzaldehyde (0.684, 5.26 mmol), and pyrrolidine (574 μL, 6.90 mmol) were used to obtain **17** as a red solid (1.18 g, 78%). Mp: 107−108 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.20 (s, 1H), 7.00 (s, 2H), 7.22 (s, 1H), 7.29−7.50 (overlapping m's, 8H), 7.54−7.62 (m, 4H), 7.69−7.73 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 79.2, 83.4, 114.1, 122.6, 126.1, 127.1, 128.1, 128.3, 128.4, 128.7, 129.4, 130.5, 132. 4, 135.0, 138.8, 137.1, 137.4, 141.6, 145.0, 147.3. Anal. calcd for $C_{26}H_{18}$: C, 94.51; H, 5.49. Found: C, 94.51; H, 5.49.

*1,3-Diphenyl-6-[4-(4-pyridyl)phenyl]fulvene (**18**).* Employing a similar procedure outlined for **7**, 1,3-diphenylcyclopentadiene (2.05 g, 9.39 mmol), 4-(4-pyridyl)benzaldehyde (2.05 g, 11.2 mmol), and pyrrolidine (1175 μL, 14.08 mmol) were used to obtain **18** as a maroon powder (2.48 g, 73%). Mp: 164−165 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.03 (d, 1H), 7.06 (m, 1H), 7.28−7.53 (overlapping m's, 9H), 7.55−7.59 (br dd, 2H), 7.70−7.79 (m, 6H), 8.69−8.73 (br dd, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 114.2, 121.4, 126.1, 127.1, 127.2, 128.1, 128.3, 128.4, 128.7, 129.4, 131.3, 135.0, 135.9, 137.2, 137.9, 138.2, 141.8, 145.1, 147.2, 147.3, 150.3. Anal. calcd for $C_{29}H_{21}N$: C, 90.83; H, 5.52; N, 3.65. Found: C, 91.10; H, 5.65; N, 3.25.

*1,3-Diphenyl-6-[4-(methyl benzoate]fulvene (**19**).* To a stirred suspension of 1,3-diphenylcyclopentadiene (2.00 g, 9.16 mmol) and methyl terephthaldehyde (1.72 g, 10.48 mmol) in absolute ethanol (50 mL) under N_2 was added pyrrolidine (1174 μL, 14.06 mmol). The reaction mixture slowly faded from pale yellow to maroon. The reaction mixture was stirred at room temperature for 138 h and then placed in an ice bath. The resulting precipitate was vacuum filtered, washed with cold absolute ethanol, and vacuum-dried to afford a dark red powder (2.68 g, 80%). Mp: 113−114 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.95 (s, 3H), 6.98 (m, 1H), 7.02 (d, 1H), 7.25 (s, 1H), 7.30−7.50 (overlapping m's, 8H), 7.66−7.73 (m, 4H), 8.09−8.14 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.1, 114.1, 126.1, 127.2, 128.3, 128.5, 128.7, 129.4, 129.8, 128.9, 130.3, 134.9, 135.8, 136.7, 141.4, 141.6, 146.0, 147.8, 166.8. Anal. calcd for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53. Found: C, 85.42; H, 5.52.

*1,3-Diphenyl-6-[4-(trimethylammonium iodide)phenyl]fulvene (**21**).* To a glass vial under N_2 were added 1,3-diphenyl-6-(4-(dimethylamino)phenyl)fulvene (0.300 g, 0.858 mmol) and excess methyl iodide (3 mL). The reaction mixture was stirred at room temperature for 24 h, and residual methyl iodide was removed under reduced pressure. The crude product was dissolved in chloroform (2 mL) and precipitated into hot stirring 90:10 hexanes:ethyl acetate. The resulting precipitate was collected via vacuum filtration, washed with excess 90:10 hexanes:ethyl acetate, and air-dried to yield a fine red powder (0.190 g, 45%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.04 (s, 9H), 6.90 (s, 1H), 7.04 (d, 1H), 7.17 (s, 1H), 7.30−7.54 (overlapping m's, 8H), 7.71−7.76 (m, 2H), 7.81−7.86 (m, 2H), 7.99−8.05 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 57.8, 113.3, 120.2, 126.3, 127.4, 128.6, 128.8, 129.3, 132.4, 133.8, 139.7, 148.4. Anal. calcd for $C_{27}H_{26}NI$: C, 65.99; H, 5.33; N, 2.85. Found: C, 65.50; H, 5.58; N, 2.80.

*1,3-Diphenyl-6-(2-naphthyl)fulvene (**22**).* To a stirred suspension of 1,3-diphenylcyclopentadiene (1.81 g, 8.29 mmol) and sodium ethoxide (0.60 g, 8.82 mmol) in absolute ethanol (40 mL) under N_2 was added 2-nathphylaldehyde (1.30 g, 8.29 mmol). The reaction mixture was heated to refluxing solvent for 5 h, during which the reaction faded from pale yellow to dark red. The reaction mixture was cooled to room temperature and then placed in an ice bath. The resulting precipitate was vacuum filtered, washed with cold absolute ethanol, and vacuum-dried to afford a crude dark brown powder (2.58 g, 87%). Mp: 167−168 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.03 (d, 1H), 7.15 (m, 1H), 7.29−7.57 (overlapping m's, 12H), 7.71−7.76 (m, 2H), 7.79−7.93 (m, 3H), 8.08 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 114.8, 126.1, 126.8, 127.1, 127.2, 127.4, 127.9, 128.1, 128.4, 128.5, 128.6, 128.7, 129.5, 131.1, 133.3, 133.4, 134.8, 135.2, 136.1, 138.7, 141.9, 144.6, 147.0. Anal. calcd for $C_{28}H_{20}$: C, 94.34; H, 5.66. Found: C, 94.27; H, 5.73.

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1,3-Diphenyl-6-(9-anthracenyl)fulvene (**23**). Employing a similar procedure outlined for **5**, 1,3-diphenylcyclopentadiene (0.530 g, 2.43 mmol), 9-anthracenylaldehyde (0.500 g, 2.43 mmol), and pyrrolidine (305 μL, 3.65 mmol) were used to obtain **23** as a bright orange powder (0.934 g, 95%). Mp: 215−218 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.21 (m, 1H), 7.10 (d, 1H), 7.19−7.30 (overlapping m's, 4H), 7.39−7.56 (overlapping m's, 9H), 7.71−7.75 (m, 2H), 8.00−8.08 (m, 3H), 8.14−8.19 (m, 2H), 8.51 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 116.2, 125.3, 126.0, 126.1, 126.3, 127.1, 127.8, 128.0, 128.5, 128.6, 128.7, 129.1, 129.3, 130.0, 131.0, 131.1, 134.8, 135.1, 135.9, 140.2, 145.9, 148.9. Anal. calcd for $C_{32}H_{22}$: C, 94.55; H, 5.45. Found: C, 94.71; H, 5.29.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01698.

ESP map data, CV voltammograms, ^{13}C, ^{1}H, and ^{19}F NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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