

## Tetraaryl Cyclopentadienones

## Tetraaryl Cyclopentadienones: Experimental and Theoretical Insights into Negative Solvatochromism and Electrochemistry

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**Abstract:** The synthesis of a series of tetraaryl cyclopentadienones comprising different substitution patterns is reported. Their photophysical and electrochemical properties are investigated by UV/Vis spectroscopy and cyclic voltammetry as well as by supporting quantum chemical simulations and reveal a distinct effect of substituents on the redox behavior of the molecules as well as the absorption properties of this class of compounds. While electrochemical data display a shift in reduction

## Introduction

The electronic nature of cyclopentadienones (CPDs) comprising a polarized C=O bond and a reactive cyclopentadiene ring renders a rich chemistry, accessible for long known oxidation, reduction or halogenation reactions.<sup>[1]</sup> Yet, recent developments in functionalization of CPDs towards molecules suitable for materials science applications or in catalysis<sup>[2,3]</sup> underline the versatility and unique properties of this class of compounds. Perhaps the most prominent transformation is the suitability of CPDs for Diels-Alder reactions as dienophiles leading to polyaromatic hydrocarbons. Following a subsequent dehydrogenation route, extended  $\pi$ -conjugated systems such as nanographenes are obtained.<sup>[4-7]</sup> Apart from extensive synthetic efforts, the cyclopentadiene core and related heterocyclic fulvenes such as CPDs have served as valuable molecules for theoretical investigations on the concept of (anti-)aromaticity.[8-15] As such, recent charge density studies have demonstrated the antiaromatic character of the cyclopentadienone core in both unsubstituted and tetraaryl-substituted CPDs with an unchanged direction of polarity of the carbonyl group (Figure 1).<sup>[15]</sup>

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potential of up to 200 mV between the differently substituted cyclopentadienones, their photophysical investigations in differently polar solvents suggest a negative solvatochromic effect, although protic solvents induce a bathochromic shift. Crystal structure analyses of some derivatives confirm similarity with related cyclopentadienones while providing insight into intermolecular C-H···O and C-H··· $\pi$  interactions in the solid state.



Figure 1. Representation of the antiaromatic character of cyclopentadienone (left) and the electro-reduction of the molecule to the corresponding stabilized radical anion (right).

In context of synthetic accessibility, cyclopentadienone itself turned out to be highly reactive and tends to dimerize. However, many stable tetraaryl-substituted CPDs have been synthesized via Knoevenagel reaction between 1,3-diarylacetones and 1,2-diketones allowing various substituents and a modular design. Transition metal-catalyzed reactions of differently substituted alkynes with suitable precursors have been used for the efficient synthesis of CPDs as well.<sup>[1,1,6,17]</sup> Particular interest, presumably owing to their intense colors, has been devoted to the photophysical properties of CPDs. The electrochemical properties though, have been reported in only a few works mainly dealing with electro-oxidation or -reduction reactions of CPDs.<sup>[18–21]</sup> While reduction of CPDs led to a fairly stable radical anion species in absence of protons (Figure 1), electro-oxidation has been shown to yield in  $\alpha$ -pyrones.<sup>[21,22]</sup>

In the course of our efforts for the development of organic molecules acting as suitable energy storage materials,<sup>[23]</sup> we got interested in CPDs as a member of the carbonyl family, which recently turned to a promising class of energy storage compounds.<sup>[24–26]</sup> Herein, we present the synthesis of a series of tetraaryl cyclopentadienones aiming to readdress phenyl and heterocyclic substitution effects on both available electrochemical window as well as photophysical properties. As such, we examine the solvatochromic effects of these compounds with combined experimental and detailed theoretical investigations





Scheme 1. *i*) NaH, toluene, Ar, 2 h reflux; 0 °C, HCl. *ii*) AcOH, HCl, H<sub>2</sub>O, 130 °C, 18 h. *iii*)  $R^2 = {}^{t}Bu$ , EtOH, H<sub>2</sub>O, KCN, 4 h reflux. *iv*) Cu(OAc)<sub>2</sub>·H<sub>2</sub>O, NH<sub>4</sub>NO<sub>3</sub>, 80 % AcOH, 4 h reflux. *v*)  $R^2 = OMe$ , Br: 1,2-dibromoethane, THF, Mg, 2 h reflux. *vi*) 1,4-dimethylpiperazine-2,3-dione, 2 h, 55 °C; HCl (1 m), 0 °C. *vii*) EtOH, KOH, reflux; CPDs **8** & **9**: ethylene glycol, reflux, 30 min.

on the nature of electronic excitations with implicit solvation models using density functional theory (DFT) and time-dependent DFT (TDDFT) simulations.

# bond lengths exhibit values of 1.357(2) Å, 1.519(2) Å, 1.359(1) Å and 1.354(2) Å, 1.520(2) Å as well as 1.354(2) Å, respectively, which is in good agreement with similar tetra-aryl-substituted cyclopentadienones.<sup>[15]</sup>

## **Results and Discussion**

#### **Synthesis**

A modular strategy is used for the synthesis of CPDs allowing the introduction of different substituents at the cyclopentadiene core. Homocoupling of commercially available para-substituted alkyl 2-(phenyl)acetate derivatives via modification of Romer's one-pot Claisen condensation<sup>[27]</sup> gave 1,3-diarylpropanones, while benzil derivatives were accessible either via benzoin condensation and subsequent oxidation<sup>[28]</sup> or Grignard reaction of arylmagnesium bromide with 1,4-dimethylpiperazine-2,3-dione.[29] Knoevenagel condensation of the precursors in ethanolic KOH solutions gave CPDs 1-7 in good to moderate yields (see SI).<sup>[29,30,39–41,31–38]</sup> For the pyridine containing CPDs 8-9, commercially available 2,2'-pyridil was used in Knoevenagel condensation reactions.[18] In contrast to the syntheses of CPDs 1-7 shown in Scheme 1, condensations gave the monohydrated species bearing a hydroxyl group at the central cyclopentadiene ring and needed harsh conditions for the elimination of water to form the dienes. Utilization of POCl<sub>3</sub> did not give the desired products, while boiling the intermediates in ethylene glycol under reflux was successful.<sup>[42]</sup> In total, nine differently substituted CPDs were obtained, and investigated both photophysically and electrochemically.

#### **Crystal Structure Analysis**

Crystals suitable for solid-state structure determination were obtained by slow evaporation of  $CDCI_3$  from NMR samples of CPDs **1** and **3** (see Figure 2). Both molecules exhibit very similar bond lengths for the central cyclopentadienone core. The C1–O1 bond lengths are 1.212(1) Å and 1.215(1) Å for compound **CPD1** and **CPD3**, respectively. For the parent molecule and the *tert*-butyl-substituted version the C2–C3, C3–C4 and C4–C5



Figure 2. Solid-state structure of **CPD3**. Ellipsoids are drawn at the 50 % probability level and intermolecular short contacts (sum of vdW radii -0.1 Å, right) are indicated by dashed lines.

Although the tert-butyl groups enhance the size of the C3 and C4 bound aryl rings, no increased tilt for these rings with respect to the cyclopentadiene core compared to unsubstituted CPD1 was observed. This might be explained by the para-location of the tert-butyl-group; hence they do not come into close proximity with the neighboring aryl rings. This is supported by a recently published crystal structure bearing a C3 bound phenyl ring with a nitro group in meta position. It was found that this aryl ring exhibits a tilt of nearly 90° with respect to the cyclopentadienone plane.<sup>[15]</sup> Additionally, the absence of a pronounced effect of even very large para-located substituents on this torsion angle has been found in various other structures as well.<sup>[43,44]</sup> Similar to many other tetraaryl-substituted cyclopentadienones, the torsion angle of the two phenyl rings bound to the C2 and C5 is smaller than for the two rings bound to C3 and C4.<sup>[15,43-48]</sup> This can be explained by the fact, that the C2 and C5 substituents possess access to "open space" around the C=O group, whereas the C3 and C4 substituents experience steric pressure from two neighboring aryl rings.

It has been hypothesized that the relatively flat positioning of the C–O neighbored phenyl rings allows for stabilization of the partially negatively charged O atom by weak intramolecular C–H•••O interactions.<sup>[43]</sup> However for **CPD1** and **CPD3** no such



short intramolecular contacts were found. Instead, several intermolecular C–H···O and C–H··· $\pi$  interactions were observed to dominate the solid-state packing behavior of these compounds (see Figure 2). Especially for the unsubstituted tetraphenyl cyclopentadienone a pairwise stabilization of two molecules sharing coplanar cyclopentadienone rings by a multitude of these interactions was found. As these interactions are not symmetrically distributed over the molecule with respect to its central mirror plane intersecting the C1–O1 and C3–C4 bond, for every phenyl ring bound to the cyclopentadienone core a different torsion angle was detected.

Finally, it should be noted that the introduction of N-atoms into the aryl ring, resulting in **CPD8**, leads to similar solid-state structures as for the above-mentioned species. However, a network of both C–H···O as well as C–H···N short contacts contribute to the packing of **CPD8** resulting in an *anti*-conformation of the two pyridyl-rings (see *Figure S67*).

#### **Photophysical Characterization**

Absorption spectra of tetraaryl cyclopentadienones usually feature a pronounced high energetic transition at around 260 nm, herein referred to as  $\lambda_3$ , a broad transition between 320–350 nm,  $\lambda_2$ , and a less pronounced broad transition peaking mostly between 490–540 nm,  $\lambda_1$ . It has already been shown, that *para*-substitution of the two chemically different phenyl rings within symmetrical tetracyclones strongly impacts the photophysical properties of the resulting derivatives,[49,50] while pairwise symmetrical substitution has been shown to result in increased effects compared to the monosubstituted analogues.<sup>[51]</sup> Thus, the absorption properties of CPDs 1–9 offering electron donating or electron accepting characteristics were investigated in acetonitrile or benzonitrile (Figure 3). The pertinent data are summarized in Table 1. It is noteworthy, that all CPDs were non-emissive in acetonitrile solutions at ambient conditions.

**CPD1** without any substitution pattern at the periphery absorbs in a range between 250 and 650 nm, with maxima at 259, 329 and 497 nm, respectively. Substitution of the 2,5-phenyl rings with inductively electron-donating *tert*-butyl groups resulted in comparable bathochromic shifts of  $\lambda_1$  of 12–15 nm (0.06–0.07 eV) for CPDs **2**, **4** and **7**, whereas the stronger donating methoxy groups upon their mesomeric effect gave bathochromic shifts of  $\lambda_1$  of up to 41 nm (0.19 eV) in CPDs **5** and **6**. As depicted via the photophysical investigation of **CPD3**, substitution of 3,4-phenyl rings did not affect  $\lambda_1$ . However, the introduction of electron withdrawing heterocycles in these positions in CPDs **8–9** led to 6 nm (0.03 eV) hypsochromic shifts compared to their phenyl analogues.

The second-lowest energetic transition  $\lambda_2$  in the electronic spectra, in terms, was not quite affected by substitution of the 2,5-phenyl rings in **CPD2**, while for electron-donating substituents on 3,4-phenyl rings again bathochromic shifts of  $\lambda_2$  were observed.

These were in the same way stronger for methoxy groups (41 nm, 0.42 eV) compared to *tert*-butyl groups (15 nm, 0.16 eV). Bromine substituents, given the balance of –I and +M

Table 1. Absorption maxima and molar absorption coefficients for the electronic spectra of CPDs **1–9** in MeCN or benzonitrile solutions.<sup>[a]</sup>

Compound	$\lambda_3^{max}$	$\lambda_2^{\max}$	$\lambda_1^{\max}$
	$\varepsilon_{\lambda 3}$	ε <sub>λ2</sub>	$\varepsilon_{\lambda 1}$
CPD1	259	329	497
	(22600)	(5635)	(1140)
CPD2	264	327	509
	(26380)	(5460)	(1620)
CPD3	261	344	497
	(21075)	(7740)	(930)
CPD4	265	343	512
	(24670)	(8120)	(1460)
CPD5 <sup>[b]</sup>	-	370	554
		(9835)	(1458)
CPD6	273	337 <sup>[c]</sup>	537
	(22950)	(6650)	(1850)
CPD7 <sup>[b]</sup>	-	340	528
		(7838)	(1680)
CPD8	255	320	491
	(26875)	(6300)	(1460)
CPD9	260	320	504
	(26430)	(5600)	(1850)

[a] Absorption maxima are reported in nm, molar absorption coefficients in L mol<sup>-1</sup> cm<sup>-1</sup>. [b] Measurements performed in benzonitrile. [c] Shoulder with  $\lambda_{max}$  of 384 nm.

effects, seem to have no effect on peak positions here<sup>[50]</sup> (CPDs **6–7**), while electron withdrawing heterocycles led to hypsochromic shifts of  $\lambda_2$ , making them shoulders of the high-energy  $\lambda_3$  transition. These show the least impact upon substitution with bathochromic shifts up to 14 nm (0.25 eV) for **CPD6**.

The polarized nature of cyclopentadienones suggests solvatochromic effects, which were analyzed via absorption spectroscopy in solvents of different polarity (see *SI*). Quantitative ab-



Figure 3. A UV/Vis absorption spectra of CPDs **1–4** in acetonitrile. **B** UV/Vis absorption spectra of CPDs **1**, **6**, **8** and **9** in acetonitrile. **C** UV/Vis absorption spectra of CPDs **1**, **5** and **7** in benzonitrile due to low solubility in MeCN. The insets show the visible region of the spectra with  $\lambda_1^{\text{max}}$ .



sorption spectra were recorded at analogous concentrations in the range of 0.04-0.01 mM in acetonitrile/benzonitrile, chloroform and THF solutions.

Upon changing the solvent from acetonitrile to less polar THF and CHCl<sub>3</sub> bathochromic shifts, mainly of  $\lambda_1$  and  $\lambda_2$  absorption maxima were observed for all CPDs. In case of **CPD6**, the detected redshift of the  $\lambda_1$  absorption maximum was 12 nm in THF and 17 nm in chloroform, respectively (Figure 4). Moreover, for **CPD4** these solvatochromic shifts were most pronounced with 23 nm for  $\lambda_1$  and 15 nm for  $\lambda_2$  in chloroform.



Figure 4. Solvatochromic effects in the UV/Vis absorption spectra of **CPD6** in MeCN, THF and CHCl<sub>3</sub>, the inset showing the visible region with  $\lambda_2^{max}$ .

**CPD6** shows a slightly stronger  $\lambda_1$  absorption in THF, while it is comparable in MeCN and CHCl<sub>3</sub>. However, absorption in  $\lambda_2$ and potentially  $\lambda_3$  was stronger in both THF and CHCl<sub>3</sub> in about the same manner, giving a hint rather on changes in torsion angles of the phenyl rings towards the central cyclopentadiene as compared to the situation in MeCN than stabilization of the excited state by the respective solvent. The observed shifts of absorption maxima would suggest a negative solvatochromic effect leading to hypsochromic shifts of absorption maxima with increasing solvent polarity. In connection with electronic absorption measurements in different solvents, it is noteworthy, that some CPDs revealed small bands between 425–475 nm, which give rise to detailed investigations.

In order to elucidate the nature of the observed solvatochromic effect in detail, we performed DFT and TDDFT simulations for three CPDs, i.e. **CPD5**, **CPD6** and **CPD8**, within gas phase, THF and MeCN. To account for a balanced description of local as well as of charge transfer excitations, we applied the longrange corrected CAM-B3LYP<sup>[52]</sup> functional with the def2-SVP basis set.<sup>[53,54]</sup> Implicit solvent effects on equilibrium structures and excited state properties were considered by a polarizable continuum model<sup>[55,56]</sup> (THF and MeCN), see *SI* for more details regarding the computational setup.

The performed TDDFT simulations allowed to provide an unambiguous assignment of the electronic excitations underlying the measured absorption bands. This is shown exemplarily for the calculated UV/Vis spectrum of **CPD6**, see Figure 5A, while the electronic nature of the respective excitations is visualized based on the charge density differences (CDDs; Figure 5B).

The quantum chemical results clearly reveal the charge transfer character of the lowest excited singlet state, S1, while electron density is shifted upon excitation from the anisyl moieties in 2 and 5 positions to the central cyclopentadienone core. In very good agreement with the experimental results, this state is predicted by TDDFT in MeCN at 539 nm (2.30 eV), while a slight redshift is observed in THF (543 nm, 2.28 eV), see Table S5 for details. This rather unsuspected stabilization of a charge transfer state by the nonpolar THF vs. the polar MeCN can be explained by a comparison of the equilibrium structures in both solvents: As predicted by previous simulations, the energy levels of the frontier orbitals, i.e. of the  $\pi$ -system, considerably depends on the planarity of the substituted cyclopentadienones.  $^{[51a,51b]}$  Ultimately, the size of the  $\pi\mbox{-system}$  is tuned by variation of the dihedral angles between the central five-membered ring and the substituents in positions 2-5. In case of CPD6, dihedral angles of 39.8 and 38.2° are predicted in MeCN, while with 38.7 and 36.9° slightly smaller angles are observed within THF. This marginal partial planarization from the equilibrium structure in MeCN to the structure in THF enhances the overlap of the  $\pi$ -system of the fragments, which leads – in consequence - to a reduced HOMO-LUMO gap (Figure 5C) as well as to a stabilization of the S<sub>1</sub> state. Furthermore, the quantum chemical simulations allow to assign the observed absorption feature between 425–475 nm to a (semi-)dark  $n_{CO}\pi^*$ -state, S<sub>2</sub>, at 398 and 402 nm (3.11 and 3.08 eV) in MeCN and THF, respec-



Figure 5. A Simulated UV/Vis absorption spectrum of **CPD6** obtained at the TDDFT level of theory (CAM-B3LYP/def2-SVP) within gas phase (reference, in black), acetonitrile (MeCN, in red) and tetrahydrofuran (THF, in blue); implicit solvent effects were considered by a polarizable continuum model. **B** Charge density differences (CDDs) of selected singlet excitations contributing to the electronic absorption spectrum in gas phase are provided exemplarily; charge transfer occurs from red to blue. **C** Energy levels of the frontier orbitals, i.e. HOMO-1, HOMO and LUMO, of **CPD6** in gas phase, MeCN and THF, all values are shown relative to the HOMO energy of the gas phase reference system.

tively, see Figure 5B. The partial optical accessibility of this state is a consequence of the mixing with  $\pi\pi^*$  transitions; for details see Tables S5 and S6. Similar effects have been observed for the charge transfer state S<sub>3</sub> – corresponding to the  $\lambda_2$  absorption band – as well as for higher lying excited states contributing to  $\lambda_3$ . Further details on the computational results addressing ground and excited state properties of **CPD6** as well as of **CPD5** and **CPD8** are collected in the supplementary information.

It is noteworthy that qualitative measurements in the most polar methanol revealed slight bathochromic shifts, predominantly for  $\lambda_1$ . This finding would not support negative solvatochromism but might be explained due to hydrogen bonding interactions of the protic solvent with the negatively charged carbonyl oxygen in the excited state. Unfortunately, the performed (TD)DFT simulations, incorporating merely implicit solvent effects, are not suitable to analyze the interaction with protic solvents, such as methanol.

#### **Electrochemical Investigations**

The synthesized series of cyclopentadienones further allowed the investigation of the impact of different substituents on the CPDs' electronic properties. Thus, all compounds have been investigated electrochemically by means of cyclic voltammetry in acetonitrile solutions of each compound containing  $nBu_4NPF_6$ as supporting electrolyte. The voltammograms are shown in Figure 6 and the pertinent data are summarized in Table 2 (referenced against Fc<sup>+</sup>/Fc).

Each cyclopentadienone shows two redox events, both an oxidation and a reduction wave. The reduction event in all cases is a reversible process, while the oxidation is quasi- or irreversible, respectively. CPD1 shows a reduction wave at -1.28 V vs. Fc<sup>+</sup>/Fc. CPD2 and CPD3 are reduced at lower negative potentials regardless of the tert-butyl phenyl groups being at the 2,5or 3,4-positions of the cyclopentadienone core. This is intuitive as electron donating groups minimize the tendency of the molecule for taking up another electron. This trend is emphasized marginally (30 mV) by substitution of all phenyl rings with tertbutyl groups in CPD4. Substitution of all phenyl rings with methoxy groups underlines this trend as the reduction potential is further shifted to lower values by 60 mV for CPD5 (-1.41 V vs. Fc<sup>+</sup>/Fc). Keeping the substitution pattern of the 2,5positions constant (tert-butyl or methoxy) while introducing bromine functionalities at 3,4-positions seems to affect the electronic properties dramatically. As a result, CPD6 is reduced easier than CPD2 by 50 mV, the same applies for CPD7 and CPD5, as well, where the substitution of an electron-donating methoxy group with a -withdrawing bromine atom resulted in easier reducibility by 200 mV. Apparently, introduction of pyridine moieties instead of phenyl lead to lower reduction potentials for the molecule, which is intuitive as pyridines are electron deficient and take up electrons easier upon electrochemical charging. In total, variation of substitution pattern at cyclopentadienone moiety allows for shifting the reduction potential up to 200 mV within the studied series of CPDs.

While the reduction events of the CPDs suggest a rather reversible behavior, the oxidation events in all CPDs can be as-

Table 2. Cyclic voltammetry data of cyclopentadienones 1-9.

Compound	$E_{\rm ox}$ [V]	$E_{\rm red}^{1/2[a]}$ [V]	$E_{pc}-E_{pa}{}^{[\mathrm{b}]}~[\mathrm{mV}]$	$i_{pa}/i_{pc}^{[c]}$
CPD1	1.11	-1.28	87	0.99
CPD2	0.97	-1.32	88	0.99
CPD3	1.06	-1.32	83	0.99
CPD4	0.93	-1.35	95	0.97
CPD5	0.71	-1.41	90	0.92
CPD6	0.75	-1.27	78	0.91
CPD7	1.14	-1.21	115	0.99
CPD8	1.05	-1.23	75	-
CPD9	1.05	-1.24	129	0.93

[a] Half-wave potential of the redox processes. [b] Difference of reductive peak potentials. [c] Ratio of the anodic and cathodic peak currents.

signed as quasi- or irreversible under the chosen conditions. However, performing cyclic voltammetry measurements in dichloromethane led to reversible processes for oxidation of most CPDs (see *SI*).

In order to evaluate the kinetics of the reduction processes, measurements at different scan rates were employed, and electrochemical parameters were calculated to determine the reversibility of the events. Figure 7 shows exemplary the recorded voltammograms for **CPD4**, and the data for all CPDs are summarized in Table 2. The separation between the oxidation and reduction peaks of all CPDs are between 78–95 mV. Considering the theoretical value of 59 mV for a Nernstian, one-electron transfer couple, all measured data point towards a quasi-reversi-



Figure 6. Cyclic voltammograms of CPDs **1–9** (except **7**) in the order of their reduction potentials [highest (bottom) and lowest (top)] value for reduction potential. Measurements were performed in 0.02 mM MeCN solutions of each compound containing 0.1 M  $nBu_4NPF_6$  at a glassy carbon as working electrode, Pt wire as counter electrode and Ag wire as reference electrode. Scan rate: 200 mV s<sup>-1</sup>. All data referenced against Fc<sup>+</sup>/Fc.



ble event, although with our setup a peak separation of 77 mV was measured for the ferrocene couple as reference during these studies. However, the ratio of cathodic to anodic peak currents is in all cases  $\approx$  1 and the current density follows a linear fashion when correlated to the square root of the scan rate (Figure 7 and Figure 8).



Figure 7. Cyclic voltammograms of **CPD4** at different scan rates exemplary for all CPD derivatives (see SI). Peak potentials are unchanged upon different scan rates (dotted lines shall guide the eye).



Figure 8. Plot of peak current density as a function of (scan rate)<sup>1/2</sup> for **CPD4** showing a linear dependency.

## Conclusion

A series of nine tetraaryl cyclopentadienones comprising different substituents at the periphery of the aryls were successfully synthesized. The results obtained from UV/Vis spectroscopy, quantum chemical simulations and electrochemical analyses of the compounds revealed the effect of *para*-functionalization of the phenyl rings or introduction of heteroatoms on the electronic effects, especially stabilizing or destabilizing polarized excited states. Whereas the position of substituents played a pivotal role in absorption maxima shifts, this was negligible in electrochemical investigations, where the total electron density of the systems determined the redox behavior. Investigations on stabilization of the excited states by solvents indicated negative solvatochromism when using differently polar solvents. This is surprising as the dipole moment in the excited state is usually increased due to its charge transfer nature and a bathochromic shift of the absorption spectrum with increasing solvent polarity is expected. However, a partial planarization of the ground state equilibrium structure in nonpolar solvents, i.e. THF, leads to an enhanced overlap of the  $\pi$ -system and, thus to a reduced HOMO-LUMO gap and a stabilization of the S<sub>1</sub> state as predicted by (TD)DFT simulations.

Given the different substitutions within the investigated cyclopentadienone series, electrochemical analyses displayed a rational access for manipulating the redox behavior of the molecules based on the electronic nature of the substituents. As such, electron withdrawing groups lower the reduction potential of a molecule while electron donating groups require higher potentials towards reduction. Following this design, molecules with a difference of reduction potential up to 200 mV were accessed. Owing to the modular synthetic accessibility and the observed features, we will pursue the design of further functionalized cyclopentadienones and their possible use as energy storage materials.<sup>[41–43]</sup> More detailed investigations into the intriguing correlations between molecular structure and photophysical properties are underway.

## **Experimental Section**

1,3-diphenylpropan-2-one, benzil, 4,4'-dibromobenzil and 2,2'pyridil were purchased and used as delivered from Sigma-Aldrich. Reagents were of commercial grade and used without further purification. Solvents were received from commercial sources and distilled prior to use or purified and deaerated using a MBraun SPS 800 solvent purification system. NMR spectra were recorded on a Bruker Avance III HD 400 at 293 K and processed with MestReNova software (Version 12.0.0). The chemical shifts  $\delta$  are reported in parts per million (ppm). <sup>1</sup>H- and <sup>13</sup>C-NMR shifts are referenced according to the used deuterated solvent as internal standard. Constants J are presented as absolute values in Hz. For the characterization of the NMR signals the following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and dd = doubletof doublets. Elemental analysis (CHN) were measured in duplicates using a Elementar Vario MICRO cube. MALDI-TOF mass spectra were measured on a Bruker Daltonics REFLEX III equipped with a pulsed nitrogen laser ( $\lambda$  = 337 nm). Data were processes with Bruker Daltonik Compass DataAnalysisViewer software (Version 5.0). Values are given in fractions m/z. For determining molar absorption coefficients, two 20 mL stock solutions ( $4 \times 10^{-4}$  M) were freshly prepared before measurements and diluted directly into 1 cm quartz cuvettes to  $4 \times 10^{-5}$  m,  $3 \times 10^{-5}$  m,  $2 \times 10^{-5}$  m and/or  $1 \times 10^{-5}$  m respectively, using suitable Hamilton microliter syringes. Each compound was measured at least twice at three different concentrations showing linear absorption behavior. No emission was found for the CPD derivatives in MeCN under ambient conditions.

Literature-known compounds CPDs **1–8** were synthesized following standard procedures given in the SI.

**1,3-Bis(4-methoxyphenyl)propan-2-one (1c):** Synthesis was carried out upon a modified literature procedure.<sup>[27]</sup> Sodium hydride



(2.77 g, 115 mmol) was dispersed in dry toluene (11 mL) in a 50 mL Schlenk flask and methyl-2-(methoxy-phenyl)acetate (11.35 g, 10 mL, 63 mmol) was added dropwise (ca. 1 h), while a constant stream of Argon was remained. Upon complete addition, the mixture was refluxed for 2 h (75 °C). After cooling in an ice bath, it was slowly added (ca. 2 h) to an ice cold HCl (15 mL + 5 mL of H<sub>2</sub>O) under vigorous stirring. Toluene was removed under reduced pressure and glacial acetic acid, HCl and water (8:4:4 mL) added to the residue of the organic phase. The mixture was refluxed overnight at 130 °C. The hot mixture was filled into a pre-heated separating funnel, leading to rapid precipitation of the product, and extracted five times into 200 mL of hot n-hexane. Crystallization gave colorless needles. The solvent of the filtrates was removed and the residue recrystallized from ethyl acetate to increase yields to 47 % (4.09 g). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$  = 7.07 (d, J = 8.7 Hz, 4H), 6.86 (d, J = 8.7 Hz, 4H), 3.80 (s, 6H), 3.65 (s, 4H) ppm. <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$  = 206.54, 158.77, 130.60, 126.22, 114.24, 110.07, 55.34, 48.14 ppm.

**2,3,4,5-Tetraphenylcyclopentadienone (CPD1):** 50 % isolated yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$  = 7.25–7.20 (m, 12H), 7.18–7.13 (m, 4H), 6.93–6.90 (m, 4H), ppm. <sup>1</sup>H-NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C)  $\delta$  = 7.31–7.16 (m, 16H), 7.01–6.93 (m, 4H) ppm. <sup>13</sup>C-NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C)  $\delta$  = 200.84, 155.32, 133.76, 131.54, 130. 69, 129.81, 129.01, 128.52, 128.50, 128.01, 126.00 ppm. EA [%] calcd. C 90.60, H 5.24; found C 90.61, H 5.23. HRMS: expected: 384.15142, found 384.15080.

**2,5-Bis(4-***tert***-butylphenyl)-3,4-diphenylcyclopentadienone**<sup>[30,31]</sup> (**CPD2):** 74 % isolated yield. <sup>1</sup>H-NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C)  $\delta$  = 7.30–7.14 (m, 14H), 7.00–6.95 (m, 4H), 1.29 (s, 18H) ppm. <sup>13</sup>C-NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C)  $\delta$  = 201.50, 154.83, 151.09, 134.12, 130.25, 129.75, 128.78, 128.55, 128.47, 125.61, 125.49, 35.02, 31.51 ppm. EA [%] calcd. C 89.47, H 7.31; found C 89.47, H 5.88. HRMS: expected: 496.27662, found 496.27600.

**2,5-Diphenyl-3,4-bis(4-***tert***-butylphenyl)cyclopentadienone**<sup>[29,32-34]</sup> (**CPD3):** 67 % isolated yield. <sup>1</sup>H-NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C)  $\delta$  = 7.29–7.17 (m, 14H), 6.87–6.83 (m, 4H), 1.27 (s, 18H) ppm. <sup>13</sup>C-NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C)  $\delta$  = 201.05, 155.56, 152.38, 131.91, 130.74, 130.68, 129.58, 128.45, 127.79, 125.61, 125.23, 35.10, 31.46 ppm. EA [%] calcd. C 89.47, H 7.31; found C 88.97, H 6.05. HRMS: expected: 496.27662, found 496.27601.

**2,3,4,5-Tetrakis(4-***tert***-butylphenyl)cyclopentadienone**<sup>[29,32,34–37]</sup> **(CPD4):** 81 % isolated yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$  = 7.28–7.21 (m, 8H), 7.18–7.14 (m, 4H), 6.87–6.83 (m, 4H), 1.30 (s, 18H), 1.29 (s, 18H) ppm. <sup>1</sup>H-NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C)  $\delta$  = 7.35–7.29 (m, 4H), 7.26–7.19 (m, 8H), 6.94–6.87 (m, 4H), 1.34 (s, 18H), 1.31 (s, 18H) ppm. <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$  = 201.54, 154.39, 151.48, 150.15, 130.64, 129.79, 129.21, 128.26, 125.04, 124.70, 124.41, 34.78, 34.70, 31.41, 31.38 ppm. <sup>13</sup>C-NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C)  $\delta$  = 201.78, 155.18, 152.14, 150.89, 131.19, 130.30, 129.54, 128.97, 125.48, 125.24, 125.21, 35.13, 35.06, 31.61, 31.55 ppm. EA [%] calcd. C 88.76, H 8.61; found C 88.70, H 8.65. HRMS: expected: 608.40182, found 608.40125.

**2,3,4,5-Tetrakis(4-methoxyphenyl)cyclopentadienone**<sup>[38-40]</sup> **(CPD5):** 79 % isolated yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$  = 7.19 (d, *J* = 8.8 Hz, 4H), 6.86 (d, *J* = 8.6 Hz, 4H), 6.79 (d, *J* = 8.6 Hz, 4H), 6.72 (d, *J* = 8.8 Hz, 4H), 3.79 (s, 12H) ppm. <sup>1</sup>H-NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C)  $\delta$  = 7.16 (d, *J* = 8.9 Hz, 4H), 6.86 (d, *J* = 8.7 Hz, 4H), 6.79 (d, *J* = 8.7 Hz, 4H), 6.72 (d, *J* = 8.8 Hz, 4H), 3.78 (s, 6H), 3.77 (s, 6H) ppm. <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$  = 201.39, 159.73, 158.92, 152.91, 131.51, 125.85, 124.09, 123.90, 113.75, 113.55, 55.31 ppm. <sup>13</sup>C-NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C) d 201.76, 160.31, 159.49, 153.72, 131.91, 131.56, 126.32, 124.65, 124.42, 114.04, 113.90, 55.72. EA [%] calcd. C 78.55, H 5.59; found C 75.33, H 5.15. HRMS: expected: 504.19367, found 504.19310.

**2,5-Bis(4-methoxyphenyl)-3,4-bis(4-bromophenyl)cyclopentadienone**<sup>[40]</sup> (**CPD6**): 39 % isolated yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$  = 7.34 (d, *J* = 8.4 Hz, 4H), 7.15 (d, *J* = 8.8 Hz, 4H), 6.84–6.73 (m, 8H) 3.79 (s, 6H) ppm. <sup>1</sup>H-NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C)  $\delta$  = 7.35 (d, *J* = 8.5 Hz, 4H), 7.15 (d, *J* = 8.9 Hz, 4H), 6.87–6.75 (m, 8H), 3.78 (s, 6H) ppm. <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$  = 200.73, 159.35, 151.26, 132.23, 131.62, 131.50, 131.09, 125.15, 122.94, 122.83, 113.94, 55.73 ppm. <sup>13</sup>C-NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C)  $\delta$  = 201.16, 159.87, 152.03, 132.85, 131.95, 131.91, 131.56, 125.65, 123.37, 123.17, 114.21, 55.73 ppm. EA [%] calcd. C 61.82, H 3.68; found C 58.60, H 3.36. HRMS: expected: 601.99152, found 601.99095.

**2,5-Bis(4-***tert***-butylphenyl)-3,4-bis(4-***bromophenyl***)***cyclopenta-dienone<sup>[36,41]</sup> (CPD7): 42 % isolated yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, 25 °C) \delta = 7.35 (d, <i>J* = 8.5 Hz, 4H), 7.28 (d, *J* = 8.5 Hz, 4H), 7.14 (d, *J* = 8.6 Hz, 4H), 6.82 (d, *J* = 8.6 Hz, 4H), 1.30 (s, 18H) ppm. <sup>1</sup>H-NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C)  $\delta$  = 7.36 (d, *J* = 8.5 Hz, 4H), 7.31 (d, *J* = 8.5 Hz, 4H), 7.15 (d, *J* = 8.5 Hz, 4H), 6.85 (d, *J* = 8.5 Hz, 4H), 1.31 (s, 18H) ppm. <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$  = 200.46, 152.10, 150.94, 132.15, 131.59, 131.11, 129.79, 127.34, 125.60, 125.36, 123.01, 34.77, 31.36 ppm. <sup>13</sup>C-NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C)  $\delta$  = 200.81, 152.89, 151.49, 132.75, 131.94, 131.55, 130.25, 128.04, 126.18, 125.69, 123.27, 35.09, 31.52 ppm. EA [%] calcd. C 67.90, H 5.24; found C 63.31, H 4.67. HRMS: expected: 654.09559, found 654.09499.

**2,5-Diphenyl-3,4-bis(2-pyridyl)cyclopenta-3-ol-1-one**<sup>[18]</sup> **(CPO):** 1.00 g (4.72 mmol) 2,2'-pyridil and 1.32 g (6.28 mmol) 1,3-diphenylacetone were stirred under reflux in 40 mL of EtOH, then 80 mg (1.43 mmol) KOH dissolved in 10 mL of EtOH were added to the reaction mixture and stirred for another hour under reflux. The resulting white precipitate was filtered off and thoroughly washed with EtOH to get 1.20 g (3.0 mmol, 64 %) of the product as a white solid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$  = 8.41 (d, *J* = 4.8 Hz, 1H), 8.35 (d, *J* = 4.8 Hz, 1H), 7.67–7.59 (m, 2H), 7.44–7.40 (m, 6H), 7.36– 7.30 (m, 3H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.09–7.03 (m, 4H), 6.64 (s, 1H), 4.35 (s, 1H) ppm. <sup>13</sup>C-NMR (500 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$  = 205.88, 164.25, 163.69, 154.18, 148.97, 148.47, 141.71, 136.52, 136.37, 134.75, 130.76, 130.57, 130.01, 128.88, 128.61, 128.13, 127.39, 125.91, 123.50, 121.89, 121. 05, 83.63, 65.44 ppm. HRMS: expected: 404.15248, found 405.15969 [M + H].

**2,5-Diphenyl-3,4-bis(2-pyridyl)cyclopentadienone**<sup>[18,42]</sup> **(CPD8):** 0.275 g (0.68 mmol) 2,5-Diphenyl-3,4-bis(2-pyridyl)cyclopenta-3-ol-1-one (**CPO**) were stirred under reflux for 20 min in 10 mL of ethylene glycol. Upon cooling to room temperature, the formed precipitate was filtered off and recrystallized from EtOH to yield 0.132 g (0.34 mmol, 50 %) as a red solid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$  = 8.35 (m, 2H), 7.52 (m, 2H), 7.26 (m, 12H, overlay with solvent), 7.07 (m, 2H) ppm. <sup>13</sup>C-NMR (500 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$  = 200.73, 153.22, 149.02, 135.92, 130.20, 130.03, 128.18, 128.01, 126.67, 124.98, 122.41 ppm. HRMS: expected 386.14191, found 386.14140.

**2,5-Bis(4-tert-butylphenyl)-3,4-bis(2-pyridyl)cyclopentadienone (CPD9):** 0.100 g (0.47 mmol) 2,2'-pyridil and 0.172 g (0.53 mmol) 1,3-bis(4-tert-butylphenyl)propan-2-one were refluxed in 20 mL of EtOH and a solution of 8 mg (0.14 mmol) KOH in 5 mL of EtOH was added. After 1.5 h, the solvent was removed and the residue was taken up into DCM, washed with water, dried with sodium sulfate and DCM was removed. 8 mL of ethylene glycol were added and the mixture was stirred for 0.5 h under reflux. Upon cooling to room



temperature, the formed precipitate was filtered off, washed with water and recrystallized from EtOH to yield 50 mg (0.1 mmol, 29 %) as a red solid. M.p. 200 °C (dec.). <sup>1</sup>H-NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C)  $\delta$  = 8.37 (d, *J* = 4.8 Hz, 2H), 7.53 (dt, *J* = 7.74 Hz, *J* = 1.74 Hz, 2H), 7.31 (td, *J* = 8.38 Hz, *J* = 1.82 Hz, 4H), 7.19–7.17 (m, 6H), 7.12–7.09 (m, 2H), 1.30 (s, 18H) ppm. <sup>13</sup>C-NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C)  $\delta$  = 201.91, 154.06, 153.40, 151.68, 149.67, 136.25, 130.24, 128.11, 126.87, 125.66, 125.32, 122.94, 35.10, 31.53 ppm. HRMS: *calculated*: 498.26711, found 498.26666.

Deposition Numbers 1996111–1996115 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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### Tetraaryl Cyclopentadienones

Tetraaryl Cyclopentadienones: Experimental and Theoretical Insights
 into Negative Solvatochromism and Electrochemistry



Substitution at tetraaryl cyclopentadienones is known to affect the photophysical properties of the molecules. In a joint experimental and theoretical investigation, a series of differently substituted tetraaryl cyclopentadienones are studied upon so far unprecedented negative solvatochromic effect and, the impact of substituents on the electrochemical behavior.

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