

Charge Transfer

Bis(Aminoaryl) Carbon-Bridged Oligo(phenylenevinylene)s Expand the Limits of Electronic Couplings

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Abstract: Carbon-bridged bis(aminoaryl) oligo(para-phenylenevinylene)s have been prepared and their optical, electrochemical, and structural properties analyzed. Their radical cations are class III and class II mixed-valence systems, depending on the molecular size, and they show electronic couplings which are among the largest for the self-exchange reaction of purely organic molecules. In their dication states, the antiferromagnetic coupling is progressively tuned with size from quinoidal closed-shell to open-shell biradicals. The data prove that the electronic coupling in the radical cations and the singlet-triplet gap in the dications show similar small attenuation factors, thus allowing charge/spin transfer over rather large distances.

Oligo(phenylenevinylene) (OPVs) compounds are stellar molecules in organic electronics.^[1] Recently their fused and planar derivatives have been prepared by inserting carbon bridges between the phenylene and vinylene units, thus



providing carbon-bridged oligo(*para*-phenylenevinylene)s (COPVs; Scheme 1).^[2-8]

COPVs have the vinylenes embedded within bicyclo-[3.3.0]octene moieties and strain the double-bond, thus pushing the ground electronic state towards a much more electro-optically active π -conjugated C=C/C-C backbone.^[3,6] This structural motif contributes to improved molecular properties, such as low oxidation potentials and high fluorescence quantum yield ($\Phi_f \approx 1$), as well as outstanding chemical stability owing to blocking the vinylene isomerization and steric protection by the carbon-bridge substituents. These features enabled us to demonstrate their utilities in applications in photovoltaics,^[5] and more recently in organic lasers.^[7] Significantly COPVs have been reported to display very large photoinduced electron-transfer rates for excited state charge separation and recombination in a donor-COPV(bridge)acceptor configuration (Zn-COPV*n*-C₆₀ in Scheme 1), and is



Scheme 1. Most significant COPV derivatives studied. Ar = 4-octyl-phenyl, and $R = CH_3$, Ph, or Ar (*p*-octylphenyl); (see Scheme S1).

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ascribed to efficient electronic tunneling and electron-vibration coupling enabled by the COPV bridge.^[8] This study, however, has raised new questions: Does donor–acceptor charge-transfer take place in the ground electronic state of COPVs [i.e., mixed-valence (MV) behavior] as efficiently as in the photoinduced excited electronic state? How does this performance compare to other known mixed-valence systems? How significant is their size-dependent transport behavior? These questions motivated us to design new donor-bridge-donor MV molecules using COPV cores as bridges.

MV systems^[9-11] offer a unique context for the study of intramolecular charge transfer (charge delocalization) within molecules. The MV property arises after a one-electron oxidation of donor- π (bridge)-donor molecules, where a competition for the positive charge occurs between the donors through the π -conjugated bridge. Robin and Day^[12] divided MV species into two main groups: 1) class III, with full charge delocalization between the donors through the bridge, and 2) class II, where the charge resides on one of the donors and the bridge stops delocalization. In the Marcus-Hush theory,^[13] there are two main parameters that control class II/III effects: 1) the electronic coupling (V_{12}) between the two donor groups, and 2) the reorganization energy (λ_{reorg}). Both are strongly dependent on the nature of the bridge: class III MV species obey $2V_{12} > \lambda_{\text{reorg}}$, and conversely, $2V_{12} < \lambda_{\text{reorg}}$ applies for class II. In particular, designing compounds with $2V_{12} \approx$ λ_{reorg} is challenging given their borderline character. Consequently, π -conjugation, conformation, and length (donor separation) of the bridge should be carefully chosen to control the class III/II character. Intimately related to the MV behavior of the monovalent cations is the shape of the divalent dications, either bipolarons (associated with class III) or polaron pairs (associated with class II).^[14]

Here we focus on the size-dependent behavior of the COPV*n* bridges having a different number of repeating units terminated with bis(arylamino) groups [DA(COPVn); Scheme 2 and see Figure S1 in the Supporting Information].



Scheme 2. Synthesis of DA(COPVn). dba = dibenzylideneacetone.

By oxidation, the charge-transfer process or MV behavior in the ground electronic state was activated. Thus, radical cations $[DA(COPVn)^{+}]$ and dications $[DA(COPVn)^{2+}]$ of variable lengths, from a monomer to a tetramer, have been studied and the large electronic couplings in the MV cations (class III) and the large antiferromagnetic bonding in the dications (closed-shell quinoidals) have been correlated. However, when V_{12} attenuates with length, the cation of DA(COPV4) become class II and its dication an open-shell singlet diradical. Scheme 2 summarizes the synthesis of the DA(COPV*n*) units, which were obtained in good to moderate yields (62–88%) using a palladium-catalyzed amination reaction from the corresponding dibromides. Their chemical characterization (Schemes S2 and S3 and Figures S2–S16), and their electrochemical (Figures S17–S20 and Table S1), spectroelectrochemical (Figures S21–S24) and optical properties (Scheme S4, Figures S25–S29) are provided.

Absorption and photoluminescence (PL) spectra of DA-(COPVn) in Figure 1 a are considerably red-shifted compared to the open unbridged DA(OPVn). Furthermore, DA-(COPV2) discloses amplification of spontaneous emission



Figure 1. a) Absorption, PL, and ASE (shaded band) spectra of DA-(COPV2) in polystyrene. b) Electrochemically obtained UV/Vis-NIR absorption spectra of the radical cations (RC) and dications (DC, shaded bands) of DA(COPV1), DA(COPV2), DA(COPV3), and DA-(COPV4)as shown in order from the bottom to the top. c) Oxidation UV/Vis-NIR spectroelectrochemistry of DA(COPV3) in CH₂Cl₂/0.1 M nBu₄NPF₆ at 22 °C (neutral: black, radical cation: red, dication: blue, radical trication: green, and tetracation: purple). d) Electrochemically obtained EPR spectra of the radical cations of DA(COPV1) (bottom) and of DA(COPV4) (top).

(ASE) at a much longer wavelength ($\lambda_{ASE} = 534$ nm) than COPV2 ($\lambda_{ASE} = 463$ nm), and is relevant for fine tuning the spectrum of ASE emission.^[15] Regarding unsubstituted COPV3,^[3] the number of oxidations in DA(COPV3) increases and the first two anodic processes appear at lower and differentiated potentials, however in DA(COPV4), they almost collapse into one two-electron process. DA(COPV3) and DA(COPV4) display reversible electrochemical formation of up to a tetracation and pentacation, respectively. Figure 1 c shows the UV/Vis-NIR spectroelectrochemical characterization of DA(COPV3) and the identifying spectra of the four consecutive oxidation states: radical cation, dication, radical trication, and tetracation.

The UV/Vis-NIR absorption spectra of the pure radical cations (RC) were extracted from the spectroelectrochemistry data in Figures 1b and Figures S21–S24. These spectra are characterized by the presence of two main bands at 18000–15000 cm⁻¹ and at 7500–5000 cm⁻¹ (HOMO \rightarrow SOMO transition as supported by DFT computations; Table 1), which

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Table 1: Spectroscopic data of the lowest-energy band of the MV radical cations, together with inter-charge distance and electronic couplings. (See Figures S30–S38 and Tables S3–S9.)

DA(COPVn)+	$\bar{\nu}_{max}$	\mathcal{E}_{max}	$\mu_{\rm ab}$	$\Delta\!\mu_{\rm ab}$	R _{N-N}	<i>V</i> ₁₂	ΔE	$\Delta E_{\rm ST}$
	[cm ⁻¹] ^[f]	[м ⁻¹ ст ⁻¹]	[D] ^[b]	[D] ^[a]	[Å] ^[a]	[cm ⁻¹]	[eV]	[cm ⁻¹] ^[e]
n=1	7190	41 200	13.0	0.2	11.54	3600 ^[c]	0.671	618
n = 2	4820	69300	16.8	0.9	17.59	2410 ^[c]	0.591	482
n = 3	4330	80500	18.9	0.4	23.67	2170 ^[c]	0.464	356
n = 4	5010	68 600	13.3	37.4	29.76	1450 ^[d]	0.269	244

[a] From DFT calculations. [b] \pm 10%. [c] Using Equation (1). [d] Using Equation (2). [e] $\Delta E_{\text{ST}} = E_{\text{Triplet}} - E_{\text{Singlet}}$ for DA(COPVn)²⁺. [f] \pm 5%.

progressively red-shift with the chain length (except in the case of DA(COPV3)⁺⁺ \rightarrow DA(COPV4)⁺⁺). In general, in class II MV species, the lowest energy band describes an intervalence charge transfer (IV-CT) with a well-defined symmetric Gaussian shape.^[16] Conversely, for class III, this band no longer has IV-CT character and its shape is asymmetric and narrow, and are clearly the cases for n = 1-3. For these class III MV compounds, V_{12} is given by Equation (1) in Table 1. For DA(COPVn)⁺⁺ n = 1-3, DFT

$$V_{12} = \frac{\bar{v}_{max}}{2} \tag{1}$$

computations indicate a vanishing dipole-moment change between ground and excited electronic states, $\Delta \mu_{ab}$, and is typical for delocalized class III radical cations. For DA-(COPV4)⁺⁺, the lowest-energy absorption band is more symmetric and DFT gives a dipole moment difference of 37 D (see Table S9), thus revealing localized class II behavior. In this case, the electronic coupling can be calculated using the Mulliken–Hush theory^[17] [Eq. (2)] where the transition

$$V_{12} = \frac{\mu_{ab}\tilde{v}_{max}}{\Delta\mu_{12}} \text{ with } \Delta\mu_{12} = \sqrt{\Delta\mu_{ab}^2 + 4\mu_{ab}^2}$$
(2)

moment (evaluated by integration of the lowest energy absorption band; see the Supporting Information), μ_{ab} , is the projection of the adiabatic transition dipole moment of the IV-CT band onto the diabatic dipole moment difference, $\Delta \mu_{ab}$, of formally fully localized (noninteracting) diabatic states.^[18] For $\Delta \mu_{ab}$ we used the DFT computed adiabatic dipole moment difference (see the Supporting Information). In this way we evaluated $V_{12} = 1450 \text{ cm}^{-1}$ for DA(COPV4)⁺⁺, which is still quite sizable given the length ($R_{\text{N-N}} = 30 \text{ Å}$) of the compound.

In addition, for DA(COPV4)⁺ the resonance stabilization energy [Eq. (3)] gives $\Delta G_r = -844 \text{ cm}^{-1} (-105 \text{ mV})$ com-

$$\Delta G_r = -\frac{2V_{12}^2}{\lambda} \tag{3}$$

pared to the 0.065 V derived from a digital fit of the CV. The V_{12} of the compounds studied here can be compared with those having comparable N–N distances from the literature. For example, for DA(COPV1)⁺⁺, the coupling $V_{12} = 3600 \text{ cm}^{-1}$ ($R_{\text{N-N}} = 11.5 \text{ Å}$) is much larger than that of a bis(triarylamine), which has a triple bond bridging the two triarylamines and

a similar N-N distance $(V_{12} = 2400 \text{ cm}^{-1}, R_{N-N} =$ 12.5 Å).^[19] The latter has almost the same coupling as DA(COPV2)⁺ ($V_{12} = 2410 \text{ cm}^{-1}$, $R_{\text{N-N}} = 17.6 \text{ Å}$), but at a much shorter N-N distance. Likewise, for DA(COPV4)⁺ the coupling $(V_{12} = 1450 \text{ cm}^{-1})$, $R_{\rm N-N} = 29.8$ Å) is slightly larger at more than twice the N-N distance than that of a bis(triarylamine) with a diethynylbenzene bridging the two triarylamines $(V_{12} = 1000 \text{ cm}^{-1}, R_{N-N} = 12.5 \text{ Å}).^{[20]}$ Open unbridged MV radical cation homologues, DA-(OPV3) and DA(OPV4), do not even show an IV-CT band (vanishing coupling).^[21] The attenuation factor, β , in Figure 2 for DA(COPVn)⁺⁺ gives a value of 0.092 Å⁻¹, thus characterizing the superexchange behavior for charge self-exchange in their ground electronic state. For the (donor)-COPVn-(acceptor) Zn-COPVn-C₆₀ compounds with n = 1-4 (Scheme 1), a small $\beta = 0.056 \text{ Å}^{-1}$



for excited state charge separation (CS) and $\beta = 0.078 \text{ Å}^{-1}$ for

charge recombination (CR) are reported.^[8]

Figure 2. Left: representation of absorption energies for the absorptions of the neutral (N blue circles), radical cations (RC1 and RC2 squares), and dications (DC1 and DC2 red circles) versus 1/*n*; see labels in Figure 1. Right: $\ln(V_{12})$ and $\ln(\Delta E_{ST})$ versus inter-donor distance (R_{N-N} , Table 1) according to the formula: $\ln(f) = \ln(f_0) - \beta/2(R_{N-N})$, R_{N-N} where $f = V_{12}$ or $f = \Delta E_{ST}$ and β is the attenuation factor. $\Delta E_{ST} = E_{\text{Ttriplet}} - E_{\text{Singlet}}$ at the (U)B3LYP/6-31G** level.

These radical cations have also been studied by EPR (Figure 1d; see Figures S39–S41). The EPR spectrum of DA(COPV1)⁺⁺ shows a five-line spectrum which results from the coupling of the odd electron with the two terminal nitrogen nuclei in either a delocalized class III or a fast-exchange regime typical of class II species with a large V_{12} value. For the longer cations, the same is observed in their EPR spectra, thus indicating that even for the DA(COPV4)⁺⁺ class II mixed-valence species, the V_{12} coupling is large enough to feature the molecules in the fast-exchange regime of the EPR technique. For DA(COPV4)⁺⁺, an approximate energy barrier for charge transfer of $\Delta G^* = \lambda/4 - V_{12} + V_{12}^2/\lambda = 210$ cm⁻¹ is deduced and in line with a fast charge transference.

The UV/Vis-NIR electronic absorption spectra of the DA(COPVn)²⁺ are in Figure 1 b and are mainly characterized by a strong absorption band resulting from the HOMO \rightarrow LUMO excitation which appears in the middle of the two bands of the radical cation. Whereas the spectra of the cations showed an anomalous blue-shift of the IV-CT band from DA(COPV3)⁺⁺ \rightarrow DA(COPV4)⁺⁺ (e.g., transition from a delocalized class III to localized class II), the absorption spectra of

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the dications also display a distinctive feature from the trimer to the tetramer, hence, the spectrum of $DA(COPV4)^{2+}$ is composed of a new additional high-energy band at about 13300 cm⁻¹, and it is formed by a pair of bands.^[11] EPR spectra of the four dications are silent, thus indicating singlet ground electronic states.

Attempts to crystallize $DA(COPV1)^{2+}$ were unsuccessful. Instead, a molecule with methoxyphenyl groups $[DA(COPV1-OCH_3)]$ replacing hexyloxyphenyls was prepared and yielded single crystals of the dication which were suitable for X-ray analysis (Figure 3). The crystal packing



Figure 3. Top: X-ray^[25] structure of a model compound, DA(COPV1-OCH₃)²⁺, showing the disposition of the SbF₆⁻ anions and main CC distances, together with comparison of the IR/Raman spectra in dichloromethane solutions of neutral (N), radical cation (RC), and dication (DC) of DA(COPV4). Bottom: canonical forms of radical cations and dications [see the Supporting Information for a discussion on DA(COPV1)²⁺]. Lateral substitution is omitted for clarity.

shows a well-ordered distribution of the two SbF₆⁻ counteranions disposed with two fluorine atoms anchored in each benzene along the main molecular plane with distances of 3.1–3.4 Å, typical for fluoride(anion)– π interactions. The perfectly ordered anions indicates that the positive charge on the DA(COPV1-OCH₃)²⁺ core is fully delocalized. DA(COPV1-OCH₃)²⁺ has a reversed C=C/C-C path regarding its neutral state (the central vinylene bond changes by 1.349–1.413 Å on neutral–dication) and the terminal C–N bonds are strongly shortened (see Figure S42). This structure is in line with a quinoidal closed-shell dication^[22] further corroborated by its NMR active spectrum.

The anomalous pair of bands for DA(COPV4)²⁺ reveals the rupture of the well-defined quinoidal structure in DA-(COPV1-3)²⁺, which becomes either an open-shell bis(radical cation)s or polaron pair.^[22] The lowest-energy band of the polaron pair dication can be attributed to a dipole-allowed excitation which takes place between the two polarons^[23] in such a way that it coalesces in the limit of infinite separation or zero orbital overlap (the polaron-pair is reduced to two individual polarons). This behavior explains why the UV/VisNIR spectra of DA(COPV4)⁺ and DA(COPV4)²⁺ resemble each other. From the optical spectra, the energy difference between the RC2 and DC/DC2 absorption bands in DA- $(\text{COPV}n)^{+}/\text{DA}(\text{COPV}n)^{2+}$ can be defined (ΔE in Table 1). ΔE decreases with *n*, in parallel with the progressive conversion of the closed-shell quinoidal dication into an open-shell biradical.^[23] In addition, in the dications, the energy difference between the singlet ground electronic state (closed-shell or open-shell) and the low-energy-lying triplet excited state (ΔE_{ST} in Table 1) have been calculated at the DFT/(U)B3LYP/6-31G** level. ΔE_{ST} represents the antiferromagnetic bonding interaction, and it is always positive and decreases with chain-length, thus revealing that: 1) the singlet character of the ground electronic state in accordance with the silent EPR spectra, and 2) the accentuation of the biradical character in DA(COPV3)²⁺ and DA(COPV4)²⁺ because of the recovery of the aromaticity in a larger number of benzenes, and is in agreement with the findings in biradicals of unsubstituted COPV dications.^[6] $\Delta E_{\rm ST}$ is further adjusted to the logarithmic equation in Figure 2 and an attenuation factor, $\beta = 0.1 \text{ Å}^{-1}$, is obtained, and it is similar to that of V_{12} , thus emphasizing the role of the π -bridge. Indeed, V_{12} and $\Delta E_{\rm ST}$ both depend on the wavefunction overlaps in the bridge between the terminal parts, so that they have a common origin and consequently similar β value.

The comparison of the infrared and Raman spectra of these redox species (see Figure 3; see Figure S43 and Tables S9-S15) provides a unified structural vision. Vibrational spectroscopy establishes that the IR and Raman spectra display complementary features in molecules having an inversion center for the point-group symmetry. In a strict sense, these molecules do not have it because of the lateral aryl chains. However, since the relevant features are due to the π -core, this segment has a local inversion center making the IR/Ra spectra complementary, as seen in the neutral compounds in Figure 3. As in the neutrals, this criteria is also fulfilled for the IR/Ra spectra of DA(COPV4)²⁺ because of the symmetric delocalization of the two charges in the π -core. For the radical cation of DA(COPV4), the IR/Ra spectra display the same strong bands either in IR and in Raman, a non-complementary effect emerging from the rupture of symmetry by localization of the positive charge in one part of the molecule or class II localized MV species (see structures in Figure 3). Conversely, in DA(COPV1)⁺ the IR/Ra comparison in Figure S43 follows the complementary effect for the three redox states, thus indicating the existence of a fully delocalized positive charge in the π -path of DA(COPV1)⁺, and is in agreement with a class III MV species and a full closed quinoidal structure in DA(COPV1)²⁺. The Raman spectra provide an additional piece of information regarding the structures of the charged species.^[6,24] From DA- $(COPV1)^{+} \rightarrow DA(COPV1)^{2+}$ the main Raman band at 1600 cm^{-1} [due to the v(C=C) modes of the benzenes] varies as $1596 \rightarrow 1592 \text{ cm}^{-1}$, a frequency downshift resulting from the enlargement of the quinoidal structure. However, on $DA(COPV4)^{+} \rightarrow DA(COPV4)^{2+}$, these bands upshift from $1587 \rightarrow 1592 \text{ cm}^{-1}$, thus revealing the transformation of the dication towards a pseudoaromatic structure.^[6]

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In summary, a new series of carbon-bridged bis(aminoaryl) oligo(para-phenylenevinylene)s have been prepared. As radical cations, they show the largest electronic couplings among the mixed-valence oligo(phenylenevinylene) series and in related purely organic systems of comparable πelectron size.^[14] The planar, rigid, and strained COPV core allows greater distances for the self-exchange electron-transfer reaction. The short and medium dications exhibit a strong antiferromagnetic coupling for all their electrons in the ground electronic state, thus imposing a closed-shell quinoidal structure. In the longest dication, DA(COPV4)²⁺, the antiferromagnetic exchange is weakened and leads to the development of a singlet open-shell biradicaloid ground electronic state. In contrast, large V_{12} and $\Delta E_{\rm ST}$ values dictate, respectively, full delocalized class III MV radical cations and full quinoidal dications, whereas their diminution transform into localized class II MV cations and open-shell biradical dications. Furthermore, the small attenuation factors permit the expansion of the electronic stimuli to rather large spatial limits. The discovery of molecular platforms, where charge and spin transfer could cover increasingly greater distances, is a key aspect in the field on single-molecular conductance and also in the design of more efficient semiconductors in organic electronics. For these fields, the COPV compounds are promising new candidates.

Acknowledgments

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Conflict of interest

The authors declare no conflict of interest.

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Communications

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Bis(Aminoaryl) Carbon-Bridged Oligo(phenylenevinylene)s Expand the Limits of Electronic Couplings



Bridge the gap: Electronic communication (charge transfer and spin coupling) over long covalent distances are achieved by using "pole-like" carbon-bridges between oligophenylene and vinylene units. This communication is demonstrated by using bis(triarylamine)-substituted carbon-bridged oligo(*para*-phenylenevinylene) cores in their radical cation and dication states.

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