FULL PAPER

Understanding the Unconventional Effects of Halogenation on the Luminescent Properties of Oligo(Phenylene Vinylene) Molecules

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Abstract: It is commonly known that halogenation tends to decrease the luminescence quantum yield of an organic dye, owing to the high electronegativity and heavy-atom effect of the halogen atom. However, based on an investigation of the effects of halogenation on the luminescence of the oligo(phenylene vinylene) (OPV) framework, we demonstrate that halogenation can have positive impact on the solid-state fluorescence and electrochemiluminescence (ECL) properties of OPV derivatives. The chlorinated OPV exhibits a very high solid-state fluorescence quantum yield (91%), whilst the brominated analogue gives the highest ECL emission intensity.

Keywords: density functional calculations • halogenation • luminescence • molecular packing • oligomers

Time-dependent density functional theory calculations, natural bond orbital analysis, and natural transition orbital analysis were performed to assist the understanding of the origin of these positive halogenation effects, which provide insight into the rational design of highly luminescent halogenated organic materials for solid-state devices and ECL applications.

Introduction

Halogenation is a very important method for the design of functional conjugated molecules and it can be used to tune various molecular properties, such as the energy levels of the molecular orbitals (MOs), bandgap, and solid-state packing.^[1] A large number of halogenated conjugate organic molecules have been reported for potential applications in the fields of organic electronic and optoelectronics, such as organic field-effect transistors (OFETs)^[1a,2] and photovolta-ics.^[3]

However, halogenation is generally avoided in the design of luminescent materials with high quantum yields (QYs) for several reasons. The heavy-atom effect (HAE) is one of the most well-known halogenation effects on the luminescent properties of organic molecules, which suggests that halogen atoms promote singlet-triplet conversion, thereby

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resulting in fluorescence quenching.^[4] This effect works by enhancing the spin-orbit coupling between the excited-state electrons of a compound and the massive nucleus of the heavy atom. Such an effect is proportional to Z^4 , where Z is the atomic number. Therefore, heavy halogen atoms may significantly decrease the fluorescence QY and excited-state lifetime of a molecule. Although the HAE increases the probability of intersystem crossing and results in more molecules occupying the triplet excitation state, it is impractical for enhancing the phosphorescence of organic molecules because the highly bonded nature of electrons in organic materials leaves them little freedom and less impetus to emit from triplet states at room temperature. Moreover, the high electronegativity of F, Cl, and Br atoms has been reported to decrease the QY by withdrawing electron density from the conjugated structure.^[5] Therefore, the common conclusion is that halogenation is a negative factor in determining the luminescence properties of organic dyes.

Recently, some investigations have shown that halogen atoms affect the luminescence properties of organic materials in a more-complicated manner than just through conventional HAEs, for example the recent discovery of crystallization-induced phosphorescence (CIP)^[6] and the "directed" heavy atom effect (DHAE).^[7] These reports have shown that, by designing chromospheres that contain triplet-producing aromatic aldehydes and triplet-promoting bromine atoms, crystal-state halogen-bonding interactions can produce highly efficient organic solid-state phosphorescence at room temperature. Würthner and co-workers reported an unexpected increase in the fluorescence QY of a series of halogenated squaraines.^[8] Duan and co-workers demonstrat-

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ed a tuning of the fluorescence emission of a single chromophore molecule through different halogen- and hydrogenbonding interactions.^[9] These recent works have indicated that more investigations are needed to gain a deeper insight into the effects of halogenation on the fluorescence properties of organic molecules and to identify possible positive effects that may benefit future materials design.

Herein, we report a combined experimental and theoretical investigation on a series of halogenated oligo(phenylene vinylene) (OPV) molecules. The OPV backbone was selected as a model structure because it is a highly fluorescence chromophore that is widely used in various optoelectronic applications.^[10] Previously, we reported that an appropriately modified OPV molecule may exhibit high solid-state fluorescence and stimulated emissions.^[11] Herein, four model compounds (Scheme 1) were synthesized and their optical



Scheme 1. Structures of the four OPV molecules that were used in this study.

properties, both in solution and in the solid state, as well as their electrochemiluminescence (ECL), were studied and compared. Aided by theoretical calculations, detailed mechanisms on how the different halogen atoms affect the luminescence properties of the OPV backbone are proposed.

This report is organized into three sections. First, the spectroscopic properties of these compounds in dilute solution are discussed. Theoretical calculations, including time-dependent density functional theory (TD-DFT), natural bond orbital (NBO) analysis, and natural transition orbital (NTO) analysis are performed to investigate the effects of halogenation on the optical properties of these

Results and Discussion

Electronic Properties in Solution

The experimental absorption and emission spectra of the four OPV molecules as dilute solutions in THF are shown in Figure 1 a; the key parameters are summarized in Table 1. To assist the analysis, the absorption and emission properties of the OPVs were also studied by TD-DFT simulations. The simulated spectra (Figure 1b) are in good agreement with the experimental ones. Notably, the absolute values of the transition energies are systematically underestimated in the theoretical calculations, consistent with previous reports.^[12] The linear fitting to the calculated and experimental transition energies shows good linearity, with a small systematic error of 0.3 eV, thus indicating that the simulation is reliable. The calculations indicate that the main electronic transition for these four molecules is the HOMO \rightarrow LUMO transition. which can also be attributed to the $\pi \rightarrow \pi^*$ transition. The excited state in this transition is the first singlet excitation state (S_1) . The highest-energy absorption peak is due to the transition from the ground state to the second singlet excitation state (S_2) , which mainly corresponds to the HOMO−1→LUMO electronic transition.

The absorption spectra of all of the OPV molecules are very similar, with two prominent absorptions within the



Figure 1. Absorption and fluorescence spectra of OPV-H and OPV-X (X = F, Cl, Br) molecules a) in THF and b) obtained from theoretical calculations. Inset shows a linear fitting to the calculated and experimental energies, including the energies of the two absorption peaks and the emission peak.

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molecules. Second, the luminescence properties of these OPV molecules in the solid state are studied and the correlation between their fluorescence properties and molecular packing in the crystal is discussed. Finally, we discuss the ECL behavior of three model OPV-X molecules under electrochemical conditions. range 2.2–4.5 eV. The lowest electronic transition $(S_0 \rightarrow S_1)^{[13]}$ gives a maximum absorption band at about 3.1 eV and the $S_0 \rightarrow S_2$ transition gives a slightly weaker band at about 3.8 eV. For OPV-H, OPV-F, OPV-Cl, and OPV-Br, the $S_0 \rightarrow$ S_1 transition occurs at 3.15, 3.18, 3.12, and 3.11 eV, respectively. Compared with OPV-H, OPV-F exhibits a higher $S_0 \rightarrow S_1$ transition energy, whereas OPV-Cl and OPV-Br show lower transition energies, thus indicating that the halo-

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Table 1. Spectroscopic parameters of the four molecules as obtained from experimental observations in solution and theoretical calculations based on TD-DFT methods.^[a]

	$E_{ m exp}^{ m abs}$	$E_{ m exp}^{ m abs'}$	$E_{ m exp}^{ m em}$	$E_{ m theor}^{ m abs}$	$E_{ m theor}^{ m abs}$	$E_{ m theor}^{ m em}$	$\mu_{ m ge}$	$\mu_{\mathrm{ge'}}$	$\mu_{\mathrm{e}^*\mathrm{g}}$	τ	$arPhi_{ m sol}$	$k_{ m r}$	$k_{ m nr}$
OPV-H	3.15	3.83	2.81	2.80	3.49	2.51	4.46	1.89	4.94	1.74	0.93	0.53	0.045
OPV-F	3.18	3.84	2.83	2.83	3.51	2.52	4.83	1.88	4.92	1.78	0.77	0.43	0.13
OPV-Cl	3.12	3.76	2.77	2.74	3.43	2.45	4.79	2.00	5.32	1.70	0.95	0.56	0.029
OPV-Br	3.11	3.75	2.76	2.73	3.42	2.44	4.93	2.00	5.48	1.31	0.60	0.46	0.31

[a] Experimental (E_{exp}) and calculated vertical-transition energies (E_{theor}) of the lowest- $(E^{abs}, in eV)$ and higher-energy allowed excited states $(E^{abs}, in eV)$; energy of the maximum of the fluorescence band $(E^{em}, in eV)$; transition dipole moments to the lowest- (μ_{ge}) and higher-energy excited states (μ_{ge}) and transition dipole moments between the optimized excited state and the ground state (μ_{e^*g}) , which defines the radiative decay rate; the fluorescence lifetime $(\tau, in ns)$; and the absolute fluorescence quantum yield (Φ) . The latter two columns show the rate constant for radiative deactivation, $S_1 \rightarrow S_0$ $(k_r, in ns^{-1})$, and the rate constant for non-radiative deactivation $(k_{nr}, in ns^{-1})$.

gen atoms have different effects on the molecular orbitals of the OPV backbone. The emission spectra of these four molecules show maximum emission energies at 2.81, 2.83, 2.77, and 2.76 eV for OPV-H, OPV-F, OPV-Cl, and OPV-Br, respectively. The order of the emission energies is consistent with the order of their maximum absorption energies, thus suggesting that the halogen atoms affect the electronic structures of the backbone in both the ground and excited states. The influence of the halogen atoms on the electronic structures of both the ground and excited states was confirmed by the calculated wavefunctions of the MOs (see the Supporting Information, Figure 1). The electron density around the halogen atom increases in the order OPV-F < OPV-Cl < OPV-Br and all of the orbitals that are involved in these transitions are affected by the halogen atoms.

Moreover, the calculations reveal that the optimized structures of OPV-H, OPV-Cl, and OPV-Br adopt a planar conformation, whereas OPV-F adopts a non-planar conformation, with a dihedral angle of 16° between the terminal and central benzene rings. Therefore, the higher $S_0 \rightarrow S_1$ transition energy for OPV-F compared with all of the other molecules is mainly due to its non-planar conformation.

The nature of the carbon-halogen (C-X) bonds in these OPVs were investigated by using natural bond orbital (NBO) analysis, which considered a multielectron molecular wavefunction in terms of localized electron-pair "bonding" units. The NBO diagrams show increased electron density

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around the C-X bonds in the order OPV-F < OPV-Cl < OPV-Br, similar to the results of the MO analysis. Owing to the increased size of the bonding orbitals, that is, 2s2p, 3s3p, and 4s4p for F, Cl, and Br, respectively, the size of C-X orbitals increased in the same sequence. In the C-X bond, the natural electron configurations of the C atoms are sp^{3.46}, sp^{3.34}, and sp^{3.49} for OPV-F, OPV-Cl, and OPV-Br, respectively, where the numbers represent the composition of the p orbital in the hybridized orbital. Notably, the natural electron configuration as calculated from the NBO analysis is different from the terms of hybridization in fundamental organic chemistry.^[14] For comparison, in the terminal benzene group of OPV-H, the natural electron configuration at the C atom in the same position is sp^{2.31}. The natural electron configurations of OPV-X clearly have a larger p-orbital component, which can be attributed to the polarization effect of the halogen atoms. The configurations of the F, Cl, and Br atoms are sp^{2.42}, sp^{4.71}, and sp^{6.30}, respectively.

The contour maps in Figure 2b suggest that, with increasing size of the halogen atom, the bonding orbitals extend further towards the carbon-atom side of the molecule, that is, the C–C *anti* bond around the benzene rings, thus indicating a greater contribution to the π system of the OPV backbone. The orbital extension can be evaluated by second-order Fock matrix analysis. The interactions result in a loss of occupancy from the localized NBO of the idealized Lewis structures into an empty non-Lewis orbital.^[15] The stabiliza-



Figure 2. a) NBO diagrams of the C–X bonds in OPV-F, OPV-Cl, and OPV-Br at a density of 0.09 and b) the corresponding contour-line maps. c) Natural bonding configuration of the C–X bonds.

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tion energies (E2) that are associated with delocalization from the C–X bond to the C–C *anti* bond, are calculated to be 3.2, 4.6, and 5.7 Kcalmol⁻¹ for OPV-F, OPV-Cl, and OPV-Br, respectively. Such an increase in E2 can be attributed to four reasons: First, the orbital size increases, owing to the increase in the size of the halogen atoms. Second, as shown from the above configuration calculations, the p-orbital component increases with increasing halogen-atom size. Third, a small part of the d orbitals participates in the bonding for C–Cl and C–Br and the d orbital can extend to the orbitals of the C–C *anti* bond (Figure 2c). Fourth, the electronegativity decreases from F to Br and, hence, the electron-withdrawing effect decreases.

In the OPV chromophore, the double bonds are more susceptible to the influence of the substituents than the benezene rings. Therefore, we studied the effects of halogenation on the deviation angles of the double bonds. In the results of the angular properties of the natural hybrid orbitals, the deviation angle represents the angle between the bonding orbital and the line of the bonded nuclei.^[14] The ideal deviation angle for a C=C double bond is 90°, which means that the two p orbitals are perpendicular to the line between two carbon atoms. Deviation of the orientation of the p orbital from the ideal angle causes a decrease in its strength. The π -orbital-deviation angles for the double bonds in OPV-H, F, Cl, and Br are 90, 88.3, 89.5, and 89.9°, respectively. Fluorination gives the largest change in the deviation angle, whilst OPV-Br had an almost-ideal 90° deviation angle.

Briefly, the NBO analysis reveals that the C–X bond affect the molecular conjugation in two ways: 1) The electron cloud from the halogen atoms extends to the aromatic rings; 2) the π -orbital-deviation angles of the C=C double bonds are influenced by the halogen atoms. These effects have rarely been discussed in previous investigations.

Halogenation has a significant impact on the fluorescence properties of the OPVs. The fluorescence QY of the OPV-H backbone in solution is very high (95%). However, OPV-F shows a much lower QY (77%). The decrease in QY upon halogenation is generally attributed to the high electronegativity of the halogen atoms.^[5] However, this NBO analysis suggests that the lowest π -orbital-deviation angle of the C= C double bond in OPV-F could be a major reason for the decrease in QY.

The QY of OPV-Br is about 60%, even lower than that of OPV-F. NBO analysis suggests that OPV-Br has an ideal π -orbital-deviation angle of the C=C double bond, that is, good conjugation. Moreover, the dorbital of the Br atom extends over the molecule, which should be beneficial for the fluorescence properties. However, the strong HAE from the Br atoms overwhelms the above two positive factors and affords a significant decrease in the QY.

In contrast to OPV-F and OPV-Br, OPV-Cl shows an unexpectedly high QY of 95%, thus indicating that chlorination does not decrease the fluorescence properties of the OPV-H backbone in this case. Given that the deviation angles as calculated from the NBO analysis is slightly lower than the ideal value and the HAE from the Cl atom, it is reasonable to expect that OPV-Cl would show a somewhat lower QY than OPV-H. NBO analysis of the C–Cl bond (Figure 2) suggests that the d orbital of the Cl atom can extend to the antibonding orbital of the C atom and increase the molecular conjugation. Therefore, the high QY of OPV-Cl suggests that the extension of the Cl d orbital has a stronger positive impact on the fluorescence properties than the negative influence factors, such as HAE, thereby resulting in an overall high QY of OPV-Cl.

Time-resolved photoluminescence (TRPL) measurements were performed for the four molecules. The fluorescence lifetime of OPV-H is 1.74 ns, close to reported vales for similar molecules.^[16] The lifetimes of OPV-F, OPV-Cl, and OPV-Br are 1.78, 1.70, and 1.31 ns, respectively. The lifetime provides information regarding the de-excitation process. From the lifetime measurements and the QYs, the rate constants for the radiative (k_r) and non-radiative processes (k_{nr}) were calculated (Table 1). The k_r for OPV-H, OPV-F, OPV-Cl, and OPV-Br are 0.53, 0.43, 0.56, and 0.46 ns⁻¹, respectively.

For a molecule in dilute solution, the de-excitation process can be described by the molecule exciton model. We performed natural transition orbital (NTO) analysis to obtain the "real" picture of the excited states, in which the excited "particle" and the empty "hole" can be described and analyzed.^[17] The calculated NTOs of the brightest excited states are shown in the Supporting Information, Figure S2. The NTOs of these molecules are different from the MOs as obtained from the TD-DFT calculations. The distinct difference between the NTOs and the MOs is at the halogen atoms. In the MOs, there is more electron density around the halogen atom in the HOMO than the LUMO, owing to the electron-withdrawing nature of the halogen atoms. However, the NTOs show less difference between the "hole" and the "electron" around the halogen atoms. Overlapping of the orbitals of the ground and excited states is known to be a key factor in the probability of electronic transition. The NTO results suggest that the lone-pair electrons of the halogen atoms participate in the excited states. The halogen atoms are increasingly involved in the exited state in the order OPV-F < OPV-Cl < OPV-Br.

The excited-state-to-ground-state transition dipole moment (μ_{e^*g}) was also obtained by NTO analysis. The relationship between the transition dipole moment and the radiative-decay rate is non-trivial, based on the Strickler-Berg equation.^[18] However, considering the similar spectroscopic properties in these four molecules, the enhanced transition dipole moment for the emissive state should lead to faster radiative-decay rates.^[19] That is, a larger transition moment generally results in a higher k_r .^[20] The transition moments as calculated for OPV-H, OPV-F, and OPV-Cl are 4.94, 4.92, and 5.32, respectively, which correspond to their experimental radiative rates. Also, the k_{nr} for OPV-F is larger than those of OPV-H and OPV-Cl, which can be attributed to the non-planar conformation and high electronegativity of the F atom. However, OPV-Br exhibits the largest calculated transition dipole moment among the four compounds,

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albeit only with a moderate experimental k_r value. This exception probably arises from the influence of ISC on the rate, which is strongly promoted by Br but is not included in our calculation model. Moreover, the lifetime of OPV-Br is much shorter than those of the other three molecules, which is expected to stem from two factors: First, the large transition moment of OPV-Br promotes a fast $S_1 \rightarrow S_0$ transition. Second, the heavy-atom effect of Br promotes the ISC progress and, hence, augments the non-radiative rates.

Optical Properties in the Solid State

OPV derivatives are potentially useful in solid-state devices, such as OLEDs,^[21] organic lasers,^[10c-c,11] and photovolatics.^[10g] Thus, we investigated the effects of halogenation on the solid-state emission properties of these OPVs. Figure 3 shows the absorption and emission spectra of the OPVs in their microcrystalline state; the key parameters are listed in Table 2. In contrast to their solution-state behavior (see above), the molecules in the crystalline state are subject to many intermolecular interactions; therefore, their emission



Figure 3. Absorption and emission spectra of the OPV molecules; the numbers 0, 1, and 2 denote the vibrational energy levels.

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properties and molecular conformations can be significantly different from those in solution.^[22]

The absorption spectra of these molecules are very similar, with a broad absorption band in the range 2.0–4.5 eV and a peak at about 2.7 eV. The absorption spectra of the OPV-X molecules have more structure in the lower-energy peaks than that of OPV-H, thus suggesting weaker intermolecular interactions in the microcrystals of OPV-X.

The emissions of the molecules are all about 2.4 eV. The emission maxima of OPV-F, OPV-Cl, and OPV-Br are at 2.42, 2.39, and 2.29 eV, respectively. The emissions from the solid samples are all bathochromically shifted compared to that in solution, but the sequence is the same as that in solution.

Because of the aggregation-caused quenching (ACQ) effect,^[23] the fluorescent QY of solid organic materials is typically much lower than that in solution. One example is perylene, which exhibits a fluorescence quantum yield of 94% in solution, but gives no emission in the solid state. To quantitatively evaluate the influence of halogen atoms on solid-state fluorescence, the parameter of fluorescence-quenching efficiency (η) is introduced, which is defined according to Equation (1).

$$\eta = (\Phi_{\rm sol} - \Phi_{\rm solid}) / \Phi_{\rm sol} \tag{1}$$

The parameter η helps to rule out the difference between the intrinsic fluorescence properties of different molecules, so that the effects of different halogen atoms on the quenching behavior of the molecules in the solid state can be compared. For OPV-H, OPV-F, OPV-Cl, and OPV-Br, $\eta = 50.5$, 11.7, 4.2, and 26.7, respectively. Clearly, OPV-X have muchsmaller quenching efficiencies than OPV-H, thus suggesting that halogenation could suppress the ACQ effect. Excitingly, the fluorescent QY of OPV-Cl in the solid state is 0.91, which is exceptionally high for solid organic materials. Solid OPV-Cl almost retains its high fluorescence QY in dilute solution, thus indicating an almost-negligible ACQ effect.

The time-resolved photoluminescence (TRPL) spectra of the OPVs in the solid state were also measured (Figure 4). Fitting to the decay curves indicates more than one exponential decay in all of the samples, which may arise from sample heterogeneity, non-exponential population decay, surface effects,^[24] etc. Assigning individual contributions by decay-curve analysis is not possible at present. Therefore,

Table 2. Experimental data of OPV-H, OPV-F, OPV-Cl, and OPV-Br in the solid state.^[a]

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	$E_{ m solid}^{ m abs}$	$E_{ m solid}^{ m em}$	$arPsi_{ m solid}$	$arPhi_{ m sol}$	η [%]	τ	$k_{ m r}$	$k_{ m nr}$	θ	Туре	d	Contact
OPV-H	2.78	2.36	0.46	0.93	50.5	1.57	0.29	0.35	34.89/22.85	lamellar	3.69	none
OPV-F	2.79	2.42	0.68	0.77	11.7	3.23	0.21	0.10	5.36	herringbone	2.96	C–H…F
OPV-Cl	2.70	2.39	0.91	0.95	4.2	1.80	0.51	0.05	68.25/44.65	herringbone	4.89 ^[b]	none
OPV-Br	2.76	2.29	0.44	0.60	26.7	1.27	0.35	0.44	13.72	herringbone	3.51	C–H…π

[a] Experimental maximum absorption energy (E^{abs} , in eV) and maximum emission energy (E^{em} , in eV); the absolute fluorescence quantum yield in the solid state (Φ_{solid}) and in solution (Φ_{sol}); the intensity-weighted average lifetime (τ , in ns); the quenching efficiency (η); the dihedral angle between the central and terminal phenyl rings (θ); and the distance between adjacent layers (d, in Å). The latter two columns show the rate constant for radiative deactivation, $S_1 \rightarrow S_0$ (k_r , in ns⁻¹), and the rate constant for non-radiative deactivation (k_{nr} , in ns⁻¹). [b] Because of the non-planar conformation of OPV-Cl, the distance was measured between the central phenyl rings.

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Figure 4. Time-resolved fluorescence spectra of the OPVs in the microcrystals. The symbols represent the experimental fluorescence-decay curves and the lines show the fitting.

the curves were simply fit to a double-exponential form to obtain the average lifetime, which represents a characteristic time constant.^[24] The average lifetimes for OPV-H, F, Cl, and Br are 1.57, 3.23, 1.80 and 1.27 ns, respectively. The average lifetime of OPV-F is much longer in the solid state than in solution (1.78 ns), whereas the average lifetimes of OPV-Cl and OPV-Br are close to those in solution. The prolonged lifetime of OPV-F can be explained by two factors: First, the vibration-relaxation process may be suppressed by the rigid structure in the crystal state, that is, suppression of the non-radiative deactivation of the excited state owing to vibrational relaxation is responsible for enhanced fluorescence emission and the longer lifetime of OPV-F compared with those in solution.^[24] Second, the pitch angle of OPV-F in the crystal is 73.5° and is assigned as H-aggregation-induced packing, in which the lowest-energy state is only weakly coupled to the ground state, thus dramatically enhancing the lifetime.^[25] The existence of exciton coupling is evident by the fact that the emission spectrum of OPV-F is structure-less (Figure 3).

The single-crystal structure of OPV-H has been reported previously.^[26] Single crystals of the OPV-X molecules were grown from solution and the crystal structures are shown in Figure 5. In general, the main factors that may induce fluorescence quenching in molecular crystals are various intermolecular interactions, which provide 3D deactivating channels, including π - π interactions, dipole-dipole interactions, Coulombic interactions, and other weak donor-acceptor interactions, such as hydrogen bonding and halogen bonding in the solid state. Moreover, potential exciton diffusion and/ or energy transfer within the aggregates may also quench the fluorescence.

OPV-H shows 1D lamellar-type packing and the long axis of the OPV-H molecules are almost parallel to one other in the crystal. The lamellar-type packing of OPV-H is favorable for dipole–dipole and charge-transfer interactions, thereby resulting in strong quenching in the solid state. Compared with the packing types of the backbone molecule OPV-H, the packing types of OPV-X are dramatically differ-



Figure 5. Molecular packing of the OPVs, viewed along the bc plane. CCDC 933885 (OPV-F), CCDC 933886 (OPV-Cl), and CCDC 933887 (OPV-Br) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

ent. All of the OPV-X molecules exhibit herringbone-type packing, owing to the polarity that is caused by the introduction of a halogen atom. Although the three OPV-X molecules have the same packing type, they pack differently in detail, thereby resulting in different optical properties in the solid state.

In the crystal of OPV-F, a strong F…H interaction is observed between the terminal F atom and the H atom of the methoxy group in the neighboring molecule, with a F…H distance of 2.57 Å. The distance between the two molecular layers is 2.96 Å, but the strong F…H interaction results in slippage along the short axis and there is little overlap between the neighboring molecules. Moreover, the dihedral angle between two adjacent columns is 81.35°. The almostorthogonal intersection structure weakens the interactions between the columns, so that the non-radiative deactivation of the excited molecules is suppressed. As a result, the OPV-F crystals show a smaller decrease in QY ($\eta = 11.7\%$) compared to the strong quenching of OPV-H ($\eta = 50.5\%$). Overall, the solid-state fluorescence QY of OPV-F (0.68) is higher than that of OPV-H (0.46).

OPV-Cl exhibits the best solid-state fluorescence properties of all four OPVs, with a QY in the solid state as high as 0.91. Moreover, the $k_{\rm nr}$ value is almost as small in the solid state as in solution, which suggests a very small ACQ effect. This superior property is associated with its unique molecular packing in the crystal. There are two coexisting molecular conformations in the crystal (see the Supporting Information, Figure 5), which have different dihedral angles between the terminal and the central benzene rings, that is, 68.25 and 44.65°. The coexistence of two crystallographically independent conformations is similar to the highly fluorescent crystals as reported by Ma and co-workers.^[27] Moreover, it has been reported, including in recent studies on the aggregation-induced emission (AIE) effect,^[28] that the nonplanar conformation is very effective at suppressing the ACO effect. Firstly, the torsional conformation enhances the steric hindrance between adjacent molecules. The distance between the central benzene rings of molecules in the two

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molecular layers is 4.89 Å, which is much longer than the π - π distance. The interaction between transition dipole moments is also suppressed by the long distance and the nonparallel dipole moments of two adjacent molecules. Secondly, the dihedral angle between any two nearby terminal benzene rings is 69.2°, so that there is no π - π packing between the terminal benzene groups. Moreover, there are no $CH-\pi$ interactions because the shortest distance between the side CH unit and the nearby benzene ring is 3.16 Å, which is larger than the CH $-\pi$ distance (typically < 3.0 Å).^[29] Thirdly, the calculated energy levels (HOMO/LUMO) for the two coexisting molecular conformations are different, that is, -1.72/-5.40 eV and -2.07/-5.39 eV, respectively. It is known from Marcus-Hush theory that the effective intermolecular transfer integral is decreased if there is an energy difference between the two adjacent molecules. Therefore, the energy difference between the two different conformations prevents energy transfer between neighboring molecules and suppresses the fluorescent quenching from intermolecular energy transfer.

The fluorescence QY of OPV-Br in the solid state is only 0.44, which is the lowest of the four OPVs. This low QY can be attributed to two reasons: First, as discussed above, the intrinsic QY of OPV-Br, as measured in solution, is the lowest, owing to the heavy-atom effect. Second, the crystal of OPV-Br exhibits the highest η value (26.7%) of the three OPV-X molecules. The high η value is attributed to $\pi - \pi$ interactions between the OPV-Br molecules. In the crystal, the distance between the two molecular layers is only 3.5 Å and the benzene ring overlays with the double bond of the adjacent molecule, thus allowing $\pi - \pi$ interactions to occur. Furthermore, in the crystal, the fluorescence of one OPV-Br molecule is not only quenched by its own Br atoms, but also by the Br atoms in the nearby molecules in a process that is similar to the external heavy-atom effect in solution.^[30]

Electrochemiluminescence Properties

The effects of the halogen atoms on the electrogenerated chemiluminescence (ECL) have also been studied. Unlike the photoluminescence method, ECL is electrochemically generated and allows us to understand the light-emitting characteristics of a chromosphere.^[31] A general route for ECL generation from the OPVs is proposed in Equations (2)–(5) to help understand the light-emitting mechanism of the chromospheres in an electrochemical cell.

$$OPV - e^- \rightarrow OPV^{+}$$
 (2)

$$OPV + e^- \to OPV^{-} \tag{3}$$

$$OPV^{\bullet+} + OPV^{\bullet-} \to OPV^* \tag{4}$$

$$OPV^* \to OPV + h\nu$$
 (5)

First, the OPV molecule is oxidized to generate a radical cation under a positive bias [Eq. (2)] and then reduced to

produce the radical anion of OPV by scanning the same working electrode potential towards the negative direction [Eq. (3)]. The formed radical anions and cations are annihilated to form the excited state of OPV [Eq. (4)], followed by radiative decay [Eq. (5)] to give off light. As shown in Figure 6, we obtained intense ECL of OPV-Cl at about



Figure 6. CV and ECL spectra of 0.24 mgmL^{-1} OPV-Cl in MeCN with 0.1 M tetrabutylammonium hexafluorophosphate (TBA+PF₆). Scan rate: 25 mVs^{-1} .

-2.0 V (versus Ag QRE) after completing a linear potential scan from 0.0 to 2.0 V. ECL generation requires both energetic species OPV⁻⁻ and OPV⁺⁺ to have adequate energy for producing the excited states of OPV; therefore, no ECL was observed when the electrode potential was only scanned within the range of 0.0 and -2.0 V or 0.0 and 2.0 V. Only weak ECL was observed if OPV-Cl was first reduced and then oxidized because the reduced species appeared to be irreversibly converted into other species through a subsequent homogenous reaction, as shown by cyclic voltammetry (CV). The oxidized OPV-Cl was relatively stable for ECL generation when the electrode potential was scanned at a high scan rate.

Instead of using CV to probe the transient ECL characteristics, the electrode potential was changed stepwise between 2.0 and -2.4 V (versus Ag QRE). As shown in Figure 7, the current response follows a Cottrell decay. Pronounced ECL can only be obtained when a negative potential step of -2.4 V is applied. No ECL or only a weak ECL is observed at the positive potential step, which is consistent with the CV experiment, as shown in Figure 7. The ECL intensity at the working electrode appears to be unstable and decreases in the first ten potential-step periods before remaining stable under a balanced supply of the oxidized and reduced species. Electrode-surface passivation in the presence of ECL by-products or their polymerized species might also account for the decreased ECL.

The insert in Figure 8b shows the shape and peak position of the ECL spectra of OPV-X. The ECL spectrum of OPV-

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Figure 7. Current and ECL responses between 2.0 V and -2.4 V for 0.24 mg mL $^{-1}$ OPV-Cl in MeCN with 0.1 m TBA-PF_6.

Figure 4). All of the OPV-X molecules show ECL in the negative potential range after a positive potential scan. All of the OPVs are irreversibly reduced whilst ECL is generated. Unlike the fluorescence studies, OPV-Br was the mostefficient OPV for ECL generation under the indicated conditions as shown in Figure 8b; then, OPV-Cl is the next most efficient for ECL generation and OPV-F is the weakest. This result is completely contrary to the conventional HAE effect, as explained by the reversibility of the reduced state of the three OPVs. OPV-Br shows relatively stable reduced states and ECL can be generated from about -1.5 V, whilst OPV-F starts generating ECL above -2.0 V. The difference with the fluorescence data can also be attributed to the complex nature of ECL generation, which relies on redox reactions and mass transfer in a different electrochemical environment. The effect of the electrode surface might also account for such differences. The complex mechanism of the ECL process makes HAE less important. As

a result, the ECL intensity increases in the sequence OPV-F < OPV-Cl < OPV-Br, which is contrary to the common perception based on HAE.

Conclusions

Our investigation into the effects of halogenation on luminescence properties of organic molecules under different conditions indicates that the halogen atoms affect their emission in a complex way. In solution, OPV-Br shows a low fluorescence QY, mainly owing to a strong HAE. However, the chlorinated molecule, OPV-Cl,



Figure 8. a) CV and b) the corresponding ECL spectra of 0.14 mgmL^{-1} OPV-F, 0.24 mgmL^{-1} OPV-Cl, and 0.12 mgmL^{-1} OPV-Br in MeCN with 0.1 m TBA·PF₆. Scan rate: 25 mVs^{-1} . Inset shows the ECL spectra of OPV-X (F, Cl, and Br) in MeCN with 0.1 m TBA·PF₆. ECL was recorded for 1 min between 2.0 V and -2.4 V for six cycles.

Cl is quite consistent with the fluorescence spectrum. The difference between the ECL and fluorescence spectra can be attributed to the difference between their generation mechanisms.^[32] ECL is generated in the electrode-diffusion range close to the electrode surface, where the redox reaction is performed, whilst fluorescence is generated in the bulk solution. Spectrum broadening for OPV-F and OPV-Br is observed, which is attributed to the poor solubility of these two halogen-substituted OPVs in MeCN.^[33] The ECL intensity appears to be much lower than the fluorescence intensity because the energetic species are not stable and the yield of excited-state generation depends on other effects, such as mass transfer of these redox species. Trace amounts of contaminates might well quench the excited state in strong electrolyte.

To determine the effect of halogen atoms on the ECL intensity, the CVs and the ECL responses for all three OPV-X molecules are shown in Figure 8 (for the current responses of OPV-F and OPV-Br, see the Supporting Information, exhibits very high fluorescence QY, mainly because the d orbital of the Cl atom positively contributes to the molecular conjugation. The solid-state luminescence properties are largely determined by the molecular conformation and packing in the crystals. The microcrystals of OPV-Cl exhibit an exceptionally high solid-state fluorescence quantum yield, owing to its twisted conformation and unique molecular packing, which efficiently prohibit the ACQ process. In the ECL experiment, the OPV-Br molecule, which has the lowest fluorescence QY in solution, exhibits the highest emission intensity, thus suggesting that the complex ECL mechanism renders HAE less important. This work provides more insight into the working mechanism of halogenation effects on the luminescence properties of organic molecules under different conditions beyond the conventional consideration of HAE. This work should help the future design of new organic fluorescence materials for various applications.

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Experimental Section

Materials and Methods

The four OPV molecules were synthesized according to a one-pot method by using a classical Horner–Wadsworth–Emmons coupling reaction,^[34,35] similar to the method reported in our previous work^[11a] (for details of the synthesis, see the Supporting Information).

Absorption and Fluorescence Measurements

Steady-state absorption spectra were recorded on a T6 UV/Vis spectrometer (Purkinje General, China). Fluorescence measurements were performed on a LS55 fluorescence spectrometer (PerkinElmer, USA). Absolute fluorescence quantum yields were measured on a FLS920 fluorescence spectrometer by using an integrating sphere (Edinburgh, UK) and exciting at their maximum excitation wavelength. Time-correlated singlephoton counting (TCSPC) by using a nanosecond-pulsed LED source (376 nm, FWHM ca. 600 ps) with a 40 MHz repetition rate was employed to measure the fluorescence-time profiles. A photomultiplier tube and a counting board (PicoQuanta, PicoHarp 300, Germany) were used for signal detection.

Electrochemiluminescence Measurements

A modified 23 mm ACE-thread glass cell (ACE Glass Inc., NJ) was used for the ECL measurements. A Pt electrode and a Ag wire quasi-reference (QRE) electrode were used as the counter and reference electrodes, respectively. A bipotentiostat CHI 760C (CH Instruments, Inc., Austin, TX) was used to generate the ECL; its auxiliary signal channel input was connected to a 1931-C high-performance low-power optical meter (Newport Corporation, Irvine, CA) and the electroluminescence signal was detected by using a photomultiplier tube (PMT) and amplified. The ECL signal was measured by using a liquid-nitrogen-cooled digital CCD spectroscopy system (Acton Spec-10:100B, Princeton instruments, Trenton, NJ) through a monochromator (Acton SP-2558, Princeton instruments, Trenton, NJ).

Quantum Chemical Calculations

All of the calculations were performed by using the Gaussian 09 software package.^[36] Adiabatic TD-DFT calculations in the Kohn-Sham (KS) form was used to calculate the excited-state structures.[37] The ground states of these four molecules were optimized by using density functional theory (DFT) with the B3LYP functional (DFT/B3LYP/6-31G + + (d, p)) and the excitation energies were calculated by using time-dependent density functional theory (TD-DFT) with the B3LYP functional (DFT/ B3LYP/6-311G++(2d,2p)). Natural bond orbital (NBO) calculations were performed by using the NBO 3.1 program,^[38] as implemented in the Gaussian 09 package. NBO analysis^[39] was performed by using the optimized conformation with the B3LYP functional (DFT/B3LYP/6-31G++ (d,p)). Then, the S₁ excited states were optimized by using the restricted configuration interaction (singlet) (DFT/6-31G(++d,p)) approach and the $S_1 \rightarrow S_0$ electronic transitions from the relaxed excited states were obtained from TD-DFT calculations by using the optimized excited states as inputs with the B3LYP functional (DFT/B3LYP/6-311G + +(2d,2p)). Natural transition orbital (NTO)^[17] calculations were performed after the TD-DFT experiments to describe the physical meaning of the orbitals of the holes and electrons on the excitation states. An inhomogeneous linebroadening parameter for all of the calculations of the absorption spectra was fixed to $\Gamma = 0.17 \text{ eV}$ for all chromospheres based on a typical line width of the respective experimental spectra.^[19] The contour map of NBO was drawn by using the Multiwfn wavefunction analyzer software.[40]

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FULL PAPER

Halo jump: Typically, halogenation decreases the luminescence quantum yield of an organic dye, owing to heavy-atom effects. Herein, appropriate halogenation has a positive impact on the solid-state fluorescence and electrochemiluminescence (ECL) properties of oligo(phenylene vinylene)s (OPVs). The chlorinated OPV exhibits a very high fluorescence quantum yield (91%), whilst the brominated OPV affords the highest ECL emission intensity.



Halogenation

Chun-Lin Sun, Jun Li, Hong-Wei Geng, Hui Li, Yong Ai, Qiang Wang, Shan-Lin Pan,* Hao-Li Zhang*_____

Understanding the Unconventional Effects of Halogenation on the Luminescent Properties of Oligo(Phenylene Vinylene) Molecules