Unveiling Halogen-Bonding Interactions between a Pyridine-Functionalized Fluoroborate Dye and Perfluorohaloarenes with Fluorescence Spectroscopy

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ABSTRACT: We have studied the halogen-bonding interactions of a pyridine-functionalized fluoroborate dye with perfluorohaloarenes (C₆F₆, C₆F₅Cl, C₆F₅Br, and C₆F₅I) in the two-component-only liquid phase using fluorescence spectroscopy. Based on the results of spectroscopic measurements and electronic-structure calculations, we have confirmed the stability only for the complex between C₆F₅I and the emissive dye, and it has been demonstrated that halogen-bonding interactions are accompanied by significant Stokes shifts for the ππ* band. We also provide experimental evidence that for this complex, the emission is quenched due to a simultaneous decrease of radiative and increase of nonradiative decay rate constants upon halogen-bonding interactions.

INTRODUCTION

Studies of halogen bonding (XB) are in the limelight as many areas benefit from its properties, including crystal engineering and live sciences. More specifically, XB-based co-crystallization, construction of liquid crystals-based phosphorescent, anion transport, and sensing materials are only a few examples of many applications of those noncovalent weak intermolecular forces. A very recent study shows how important the halogen bonding is for the aggregation of photoactive compounds with attached luminoephores. Several reviews focused on XB highlight the dependence of this interaction on electron acceptors in the molecule carrying the halogen bond donor. Although XB has great potential in crystal engineering in the design of new materials, understanding its properties in solution delivers a complementary information on their nature. This was the rationale behind numerous studies in solutions, often composed of more than two constituents, which aimed at understanding the thermodynamics of the XB formation or changes in vibrational spectra induced by the XB. The fundamental aspects of XB in simple systems are nowadays well understood and the challenge lies in obtaining the full benefit of this knowledge in rational design of materials with tailored properties. In particular, modifying the optical responses of π-conjugated dyes, including their emission, by specific interactions such as XB is a particularly attractive design route. A recent study demonstrated that, for heavy-atom carrying diodo-BODIPY interacting with XB acceptors or in bromobenzaldehyde in the solid state, halogen bonding facilitates the formation of the triplet state after the photon absorption by increasing the intersystem crossing rate constant. On the other hand, in the case of anion sensing compounds, the formation of the XB complex increases the fluorescence of the probe due to rigidification of its structure or causes a serious limitation of random movements within, for example, the interlocked catenanes.

In order to fully benefit from properties of halogen-bonding interactions involving organic dyes, it is mandatory to understand the subtle changes in the electronic structure of organic compounds upon the formation of a halogen bond. Moreover, considering that the absolute value of interaction energy in complexes stabilized by XB follows the F < Cl < Br < I ordering due to different polarizabilities of halogen (fluorine is rarely involved in such interactions), hence, studying the whole series of halogen atoms delivers thorough characteristics of XB properties. The present study contributes to these efforts and aims at studying the changes in electronic absorption and emission spectra upon interactions of an emissive pyridine-functionalized dye with perfluorohaloarenes (C₆F₆, C₆F₅Cl, C₆F₅Br, and C₆F₅I) in the two-component-only liquid phase. In fact, previously it has been shown that electronic spectroscopy can be useful in the study of halogen bond in molecular complexes.

It is known that a very efficient BF₂-/BF-carrying fluorophores (similar to classical BODIPYs) hold a privileged spot due to high fluorescence quantum yields (FQYs) deriving from a rigid core in their structure. Similar rigidity, crucial for enhancing the radiative dissipation of excitation energy, is the...
characteristics of several close-relative families of dyes: boranils, ketonates, or ketoiminates. Given the excellent photophysical properties of these dyes, we designed the new compound (denoted as D) shown in Figure 1. Because the topology of the dye is crucial, during the design of D, we relied on the experience gained in some of our previous works. The structure of D was proposed to obtain a molecule prone to interactions through XB and exhibiting intramolecular charge transfer (ICT) in the lowest-lying electronic excited state. Note that, by design, the halogen bond acceptor is not the primary electron-donating moiety involved in the ICT. Because the highest fluorescence quantum yield in previously described diazines was obtained for the isomer carrying a nitrogen atom in the para position in relation to the donor-to-acceptor conjugation path (red arrow in Figure 1), in the current study, pyridin-4-yl was used as the building block. Taken together, the structural and photophysical characteristics of D should allow for the achievement of the specific goals of this study, including the following: (a) confirming the formation of a halogen bond and (b) analyzing its influence on the photophysical properties of the dye, with special emphasis on the radiative energy dissipation.

The palette of solvents used is also shown in Figure 1. The synthesis of D was carried out in a similar way to dyes presented in a previous publication by some of the present authors. The procedure is described in the Methods and Protocols, but we want to emphasize that unlike in other studies aiming at characterizing XB interactions in solutions based on absorption and emission, we used a non-competitive environment without any additional solvent. Furthermore, all spectra reported here were recorded in solvents freshly distilled under a nitrogen atmosphere.

### RESULTS AND DISCUSSION

Figures 2 and 3 show the electronic absorption and emission spectra of D in C_{6}F_{6}, C_{6}F_{5}Cl, C_{6}F_{5}Br, and C_{6}F_{5}I solvents, while the summary of the photophysical properties of such spectra is collected in Table 1.

The cut of the absorption spectra at ca. 390 and 345 nm is due to the intense absorption of C_{6}F_{5}I and C_{6}F_{5}Br, respectively. As it is expected for ICT-exhibiting molecules, the absorption spectra measured for the four used solvents have a broad absorption band without any vibrational fine structure. A clear noticeable red-shift of absorption band maximum with respect to that for C_{6}F_{6} is noticed solely for C_{6}F_{5}I. This trend is even more pronounced in the case of emission spectra, that is one finds a much broader and red-shifted band for D in C_{6}F_{5}I. Note that shifts of emission bands for other solutions are insignificant with respect to C_{6}F_{6}.

![Figure 1. Synthesis of studied emissive dye (D) and the palette of solvents. The green arrow indicates the direction of the ICT, and the red arrows indicate the direction of the donor-to-acceptor conjugation paths.](image)

![Figure 2. Normalized absorption spectra of D in C_{6}F_{6}, C_{6}F_{5}Cl, C_{6}F_{5}Br, and C_{6}F_{5}I solvents.](image)

![Figure 3. Normalized fluorescence spectra of D in C_{6}F_{6}, C_{6}F_{5}Cl, C_{6}F_{5}Br, and C_{6}F_{5}I solvents.](image)
Table 1. Photophysical Properties of D in Various Solvents Measured at r.t. and Values Marked in Bold Were Calculated at the TD-DFT Level

| solvent   | $\lambda_{abs}$ [nm] | $\epsilon$ [M$^{-1}$ cm$^{-1}$] | $\lambda_{em}$ [nm] | Stokes [cm$^{-1}$] | FQY [%] | $\tau$ [ns] | $k_1$ [$10^9$ s$^{-1}$] | $k_{nr}$ [$10^9$ s$^{-1}$] | $\chi^2$ |
|-----------|----------------------|---------------------------------|---------------------|-------------------|--------|-----------|-------------------|-------------------|--------|
| C$_6$F$_6$ | 420                  | 20,290                          | 490                 | 3400              | 35.1   | 2.91      | 0.121             | 0.223             | 1.101  |
| C$_6$F$_5$Cl | 425                 | 20,270                          | 484                 | 2870              | 39.8   | 2.97      | 0.134             | 0.203             | 1.042  |
|           | 382                  | 437                             | 3293               |                   |        |           |                   |                   |        |
| C$_6$F$_5$Br | 425                 | 20,330                          | 493                 | 3245              | 34.1   | 2.59      | 0.130             | 0.254             | 1.075  |
|           | 385                  | 454                             | 3938               |                   |        |           |                   |                   |        |
| C$_6$F$_5$I  | 430                 | 20,620                          | 539                 | 4702              | 1.4    | 0.51      | 0.027             | 1.933             | 1.364  |
|           | 388                  | 473                             | 4623               |                   |        |           |                   |                   |        |

The $\tau$ for C$_6$F$_5$I is the weighted average of two lifetimes, $\tau = 0.48$ ($\alpha = 0.94$) and $\tau = 1.01$ ns ($\alpha = 0.06$).

C$_6$F$_5$Cl/C$_6$F$_5$Br and C$_6$F$_5$I solutions at various temperatures are significant. More specifically, the spectra recorded in C$_6$F$_5$I are far more sensitive to the temperature changes than the C$_6$F$_5$Br ones. This could be rationalized by considering that C$_6$F$_5$I is the only solvent that has a stable XB interaction with the heterocyclic nitrogen atom present in the pyridin-4-yl moiety. The N···I interactions are further supported by the FTIR spectra shown in Figure S11 in the Supporting Information file and the $^1$H NMR titrations of D in C$_6$F$_5$I by C$_6$F$_5$I (Figures S12–S14, see Supporting Information file), which deliver the association constant of approximately 750 M$^{-1}$. Moreover, the XB interaction between C$_6$F$_5$I and D was confirmed by the comparison of the CIS (complexation-induced shift, in [ppm], defined as the difference between chemical shift of the respective proton in the free molecule and in the interacting molecule at the saturation conditions) for every proton in D (Figure S15). The description of the experimental procedure is available in the Methods and Protocols section, while the exemplified, stacked NMR spectrum, with labeled protons, is shown in Figures 4 and S12.

Figure 4. NMR stacked spectra for titration of D by C$_6$F$_5$I in C$_6$F$_5$ solution.

Taken together, these results confirm that D in its ground electronic state interacts specifically with C$_6$F$_5$I. It is worth highlighting that the emission for D at a low temperature is less intense than at room or elevated temperatures, a feature that is in contrast to the usual temperature effect on fluorescence. We suggest that this temperature dependence is caused by the increase of the strength of XB between D and C$_6$F$_5$I when the temperature decreases (observed even in rigid solid$^{10}$). The fluorescence lifetime measurements at room temperature (Table 1) show that the drop of fluorescence quantum yield upon C$_6$F$_5$I/D complex formation is caused by a 5-fold decrease in $k_1$ and 10-fold increase in $k_{nr}$ values.

In order to further support the experimental pieces of evidence of influence of halogen bonding on the electronic spectra of D, we performed a series of electronic-structure calculations using (time-dependent) density functional theory [(TD) DFT] with the MN15 functional and wave function-based SCS-MP2 method. The computational details are presented in the Methods and Protocols section. The geometry optimizations in the ground electronic state indicate that C$_6$F$_5$I does not form a XB with the nitrogen atom of the pyridine in D. The calculated ground-state interaction energies for the remaining complexes are shown in Table S2, and they follow the usual trend for halogen-bonded complexes, that is, the value of interaction energy for C$_6$F$_5$I/D corresponds to the most stable complex. Comparison of the interatomic distances within the N···X bridge through the different compounds in the ground and excited equilibrium geometries leads to interesting conclusions. In Table 2, the distance between the halogen atom and the nitrogen acting as a halogen bond acceptor is shown for the ground state (S$_0$) and the excited state (S$_1$) geometry.

Table 2. Bond Lengths (in Å) and Angles (in deg) for the Electronic Ground (S$_0$) and Excited State (S$_1$)

| complex       | N···X bond length (R, [Å]) | N···X–C bond angle (α, [deg]) |
|---------------|---------------------------|-------------------------------|
|               | R(S$_0$) | R(S$_1$) | R(S$_1$)–R(S$_0$) | α(S$_0$) | α(S$_1$) |
| C$_6$F$_5$Br/D | 2.8390   | 2.7164   | −0.1126            | 174.22   | 179.94   |
| C$_6$F$_5$I/D | 2.8057   | 2.6827   | −0.1230            | 179.74   | 179.66   |

Geometry optimizations were performed at the MN15/aug-cc-pVDZ(PP) level of theory.

For both states, the N···X length decreases while increasing the polarizability of the halogen involved in the interactions, following the interaction energy values. Moreover, Table 2 shows that on passing from the ground electronic state to the excited state, a shortening of N···X is observed for all complexes, with largest (smallest) shortening found for C$_6$F$_5$I/D (C$_6$F$_5$Cl/D). Table 2 also contains the angle of the halogen bond for the different compounds, and it can be observed that the stronger the interaction, the closer is the angle to 180°. The trends in DFT-based absorption spectra of all isolated complexes are in line with the experimental data. Notably, those calculations show that all compounds exhibit absorption features in the range of 380–390 nm (see Table 1). Interestingly, these results show that complex C$_6$F$_5$I/D presents a small but clear red shift in the maximum of absorption (6 nm) with respect to C$_6$F$_5$Cl/D. However, the simulated spectra of all complexes (Figure S) are very similar, a feature that supports the general rule of the larger sensibility of
emission spectra over absorption to the changes in the electronic structure of D.

Figure 5. Normalized simulated absorption (solid line) and emission (dashed line) spectra for C₆F₅Cl/D, C₆F₅Br/D, and C₆F₅I/D complexes in the gas phase at the MN15/aug-cc-pVDZ level of theory.

We have also performed TD-DFT calculations to take into account the effect of the C₆F₅ and C₆F₅ solvent polarity on emission spectra using the SMD implicit solvation model. The TD-DFT calculations predict a shift between the emission of D in both solvents of only 7 nm, indicating that the experimental shift cannot be explained considering only the effect of the solvent polarity. In order to link these observations with the electronic structure of the complexes, we determined the difference in electronic density between the excited and ground state at the ground- and excited-state geometry (Figure 6). The results show that electronic density difference, pointing toward vertical absorption, is not large, that is, the effect of the halogen bond on the absorption process is small. On the contrary, there is a significant density change over the N···I bond during the vertical emission process, explaining the sensitivity of the emission wavelength due to the formation of the halogen bond.

Figure 6. Electron density difference between the excited and ground states of the absorption (top) and emission (bottom) process for the D/C₆F₅I complex.

The trend of halogen bonding strengths (Cl < Br < I), with the latter being the one that presents a larger red shift with respect to C₆F₅/D. Another feature observed is the decrease of the intensity in the emission bands while following the halogen bond strength trend. This fact is in accordance with the measured fluorescence quantum yield. Although all these features agree between experiments and simulations, a distinct difference in the C₆F₅Br/D emission spectra is observed. From experiments, the shift of the maximum of emission in C₆F₅Br is not large, while in DFT calculations, it is more pronounced, agreeing once more with the trend of the halogen bonding strength order. To shed light on this observation, we computed the Gibbs energy (ΔG) for the formation of C₆F₅Cl/D, C₆F₅Br/D, and C₆F₅I/D complexes (Table 3), including the correction term to simulate the effect of the experimental concentration of the reactants.

Table 3. Formation Gibbs Energy (ΔG, in kcal/mol) and Formation Energy (ΔE, in kcal/mol) Calculated Using the MN15 Functional and the Aug-cc-pVDZ(PP) Basis Set

| complex | ΔG  | ΔE  |
|---------|-----|-----|
| C₆F₅Cl/D | 3.181 | -2.478 |
| C₆F₅Br/D | 0.493 | -5.017 |
| C₆F₅I/D | -1.717 | -8.029 |

The only complex that presents an exergonic complex formation due to the halogen bonding is C₆F₅I/D. Therefore, the DFT calculations suggest that only the formation of the C₆F₅I/D complex is favorable. On the contrary, in the experimental conditions, DFT calculations indicate that C₆F₅Cl/D and C₆F₅Br/D complexes are not favorable. These data support the experimental results showing the largest shifts in absorption and emission spectra for the C₆F₅I/D complex.

CONCLUSIONS

In conclusion, we have studied the halogen-bonding interactions between an emissive pyridine-functionalized fluoroborate dye and perfluorohaloarenes (C₆F₅Cl, C₆F₅Br, and C₆F₅I) in the two-component-only liquid phase. Based on the spectroscopic measurements, supported by electronic-structure calculations, we have confirmed the stability of the C₆F₅I/D complex, and it has been demonstrated that only halogen-bonding between D and C₆F₅I is accompanied by significant Stokes shifts for the ππ* band. This effect is not observed for other studied complexes. We also provided experimental evidence that in the case of the C₆F₅I/D complex, the emission is quenched due to the decrease of kₑ and increase of kₘ upon halogen-bonding interactions at a specific site of the dye. The fluorescence quantum yield is even more influenced by temperature. Even though electronic spectroscopy was more scarcely used in studies of halogen bonding in solution in comparison to other techniques, the results presented herein demonstrate that this technique can provide valuable information regarding the influence of XB on photophysical properties of dyes in the two-component-only liquid phase.

METHODS AND PROTOCOLS

Synthesis. The synthetic path shown in the article starts with the synthesis of N-(6-aminoypyridin-2-yl)-4-(dimethylamino)benzamide (mono-amide) by the reaction between 2,6-diaminopyridine and ethyl 4-(dimethylamino)benzoate in THF solution with the use of
two equivalents of sodium hydride (60% suspension in oil) as in one of our previous reports.\textsuperscript{41} The obtained mono-amide was used in the next step, i.e., during the formation of another amide moiety as follows: to a THF solution of N-(6-amino-2-yl)-4-(dimethylamino)benzamide (1.0 g, 3.9 mmol) in three-necked flask, two equivalents of NaH (ca. 0.32 g, 60% suspension in oil) was added under a dry nitrogen flow. After magnetic stirring (2 h) at boiling point, one equivalent of ester (0.59 g, 3.9 mmol, solution in 5 mL of dry THF) was added using a syringe through the septum. The mixture was heated at boiling point overnight. After cooling to r.t., the reaction was quenched with saturated, water NH\textsubscript{4}Cl solution (10 mL). The resulted mixture was evaporated to remove THF, solid mixture that precipitated from water separated, and washed gently with cold water to remove inorganic salts. The residual was recrystallized from alcohol to give 0.49 g (34.8%) of the final bis-amide. The resulted bis-amide was treated with BF\textsubscript{3} etherate (5 equiv, ca. 0.85 mL)\textsuperscript{41} in boiling toluene (20 mL) and 5 equiv of DIEA (ca. 1.1 mL) was added. After heating the reaction mixture for 5 h, the reaction was cooled and quenched with saturated, water Na\textsubscript{2}CO\textsubscript{3} solution (10 mL). The mixture was extracted with DCM, the organic layer was dried using Na\textsubscript{2}SO\textsubscript{4}, evaporated, and purified using column chromatography (elucent DCM), giving 0.16 g (30.3%) of pure D. 

**Measurements.** All of the NMR spectra were recorded using a 400 MHz Bruker spectrometer at room temperature (spectra available in the Supporting Information). Structural assignments were made with additional information from gCOSY, gHSQC, and gHMB spectrum experiments. HRMS spectrum was recorded using sector mass spectrometer AutoSpec Premier (Waters) equipped with an electron impact (EI) ion source and the EBE double focusing geometry mass spectrometer AutoSpec Premier (Waters) equipped with an electron impact (EI) ion source and the EBE double focusing geometry mass spectrometer AutoSpec Premier (Waters) equipped with an electron impact (EI) ion source and the EBE double focusing geometry mass spectrometer AutoSpec Premier (Waters) equipped with an electron impact (EI) ion source and the EBE double focusing geometry mass spectrometer AutoSpec Premier (Waters) equipped with an electron impact (EI) ion source and the EBE double focusing geometry mass spectrometer AutoSpec Premier (Waters) equipped with an electron impact (EI) ion source and the EBE double focusing geometry mass spectrometer AutoSpec Premier (Waters) equipped with an electron impact (EI) ion source and the EBE double focusing geometry mass spectrometer AutoSpec Premier (Waters) equipped with an electron impact (EI) ion source and the EBE double focusing geometry mass spectrometer AutoSpec Premier (Waters) equipped with an electron impact (EI) ion source and the EBE double focusing geometry mass spectrometer AutoSpec Premier (Waters) equipped with an electron impact (EI) ion source and the EBE double focusing geometry.
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REFERENCES

(1) Walsh, R. B.; Padgett, C. W.; Metrangolo, P.; Resnati, G.; Hanks, T. W.; Pennington, W. T. Crystal engineering through halogen bonding: complexes of nitrogen heterocycles with organic iodides. Crystal Growth Des. 2001, 1, 165−175.

(2) Mukherjee, A.; Tothadi, S.; Desiraju, G. R. Halogen bonds in crystal engineering: like hydrogen bonds yet different. Acc. Chem. Res. 2014, 47, 2514−2524.

(3) Ates, Ö. D.; Zorlu, Y.; Kannazal, S. D.; Chumakov, Y.; Gurek, A. G.; Ayhan, M. M. Halogen bonding driven crystal engineering of iodothiononitile derivatives. CrystEngComm 2018, 20, 3585−3667.

(4) Wang, W.; Zhang, Y.; Jin, W. J. Halogen bonding in room-temperature phosphorescent materials. Coord. Chem. Rev. 2020, 404, 213107.

(5) Auffinger, P.; Hays, F. A.; Westhof, E.; Ho, P. S. Halogen bonds in biological molecules. Proc. Natl. Acad. Sci. U.S.A. 2004, 101, 16789−16794.

(6) Wilcken, R.; Zimmermann, M. O.; Lange, A.; Joerger, A. C.; Auffinger, P.; Hays, F. A.; Westhof, E.; Ho, P. S. Halogen bonds in electrostatically-driven highly directional noncovalent interaction. Phys. Chem. Chem. Phys. 2010, 12, 7748−7757.

(7) Beale, T. M.; Chudzinski, M. G.; Sarwar, M. G.; Taylor, M. S. Halogen bonding in solution: thermodynamics and applications. Chem. Soc. Rev. 2013, 42, 1667−1680.

(8) Caballero, A.; Zapata, F.; White, N. G.; Costa, P. J.; Félix, V.; Beer, P. D. A halogen-bonding catenane for anion recognition and sensing. Angew. Chem., Int. Ed. 2012, 51, 1876−1880.

(9) Metrangolo, P.; Murray, J. S.; Pilati, T.; Primagi, A.; Resnati, G.; Terraneo, G. The halogen bond. Chem. Rev. 2016, 116, 2478−2601.

(10) Vaz, P. A. A. M.; Rocha, J.; Silva, A. M. S.; Guieu, S. Highly fluorescent red-light emitting bis(boranils) based on naphthalene backbone. J. Org. Chem. 2017, 82, 8234−8241.

(11) Vaz, P. A. A. M.; Rocha, J.; Silva, A. M. S.; Guieu, S. Aggregation-induced emission enhancement of chiral boranils. New J. Chem. 2018, 42, 18166−18171.

(12) Lyu, H.; Wang, D.; Cai, L.; Wang, D.-J.; Li, X.-M. Synthesis, photophysical and solvatochromic properties of diacetoxyboron.
complexes with curcumin derivatives. Spectrochim. Acta, Part A 2019, 220, 117126.

(36) Wang, J.-X.; Yu, Y.-S.; Niu, L.-Y.; Zou, B.; Wang, K.; Yang, Q.-Z. A difluoroboron \(\beta\)-diketonate based thermometer with temperature-dependent emission wavelength. Chem. Commun. 2020, 56, 6269–6272.

(37) Zhao, J.; Peng, J.; Chen, P.; Wang, H.; Xue, P.; Lu, R. Mechanofluorochromism of difluoroboron \(\beta\)-ketoiminate boron complexes functionalized with benzoxazole and benzothiazole. Dyes Pigm. 2018, 149, 276–283.

(38) Ośmiłowski, B.; Petrusevich, E. F.; Antoniak, M. A.; Grela, L.; Bin Jassar, M. A.; Nyk, M.; Luis, J. M.; Jędrzejewska, B.; Zaleśny, R.; Jacquemin, D. Controlling two-photon action cross section by changing a single heteroatom position in fluorescent dyes. J. Phys. Chem. Lett. 2020, 11, 5920–5925.

(39) Ośmiłowski, B.; Petrusevich, E. F.; Nawrot, K. C.; Paszkiewicz, B. K.; Nyk, M.; Zielak, J.; Jędrzejewska, B.; Luis, J. M.; Jacquemin, D.; Zaleśny, R. Tailoring the nonlinear absorption of fluorescent dyes by substitution at a boron center. J. Mater. Chem. C 2021, 9, 6225–6233.

(40) Forni, A.; Metrangolo, P.; Pilati, T.; Resnati, G. Halogen bond distance as a function of temperature. Cryst. Growth Des. 2004, 4, 291–295.

(41) Dziuk, B.; Ośmiłowski, B.; Zarychta, B.; Ejsmont, K.; Chęciniska, L. Symmetric Fluoroborate and its Boron Modification: Crystal and Electronic Structures. Crystals 2019, 9, 662.

(42) Kelly, C. P.; Truhlar/Cramer, C. J. Adding explicit solvent molecules to continuum solvent calculations for the calculation of aqueous acid dissociation constants. J. Phys. Chem. A 2006, 110, 2493–2499.

(43) Frisch, M. J., et al. Gaussian 16, Revision C.01; Gaussian Inc: Wallingford CT, 2016.

(44) Werner, H.-J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schütz, M. Molpro: a general-purpose quantum chemistry program package. Wiley Interdiscip. Rev.: Comput. Mol. Sci. 2012, 2, 242–253.