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# Thermally Activated Delayed Fluorescence from Ag(I) Complexes: A Route to 100% Quantum Yield at Unprecedentedly Short Decay Time

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**Supporting Information** 



ABSTRACT: The four new Ag(I) complexes Ag(phen)(P2-nCB) (1), Ag(idmp)(P2-nCB) (2), Ag(dmp)(P2-nCB) (3), and  $Ag(dbp)(P_2-nCB)$  (4) with  $P_2-nCB = bis(diphenylphosphine)$ -nido-carborane, phen = 1,10-phenanthroline, idmp = 4,7dimethyl-1,10-phenanthroline, dmp = 2,9-dimethyl-1,10-phenanthroline, and dbp = 2,9-di-n-butyl-1,10-phenanthroline were designed to demonstrate how to develop Ag(I) complexes that exhibit highly efficient thermally activated delayed fluorescence (TADF). The substituents on the 1,10-phenanthroline ligand affect the photophysical properties strongly (i) electronically via influencing the radiative rate of the  $S_1 \rightarrow S_0$  transition and (ii) structurally by rigidifying the molecular geometry with respect to geometry changes occurring in the lowest excited  $S_1$  and  $T_1$  states. The oscillator strength of the  $S_1 \leftrightarrow S_0$  transition  $f(S_1 \leftrightarrow S_0)$  an important parameter for the TADF efficiency being proportional to the radiative rate—can be increased from  $f(S_1 \leftrightarrow S_0) =$ 0.0258 for Ag(phen)(P<sub>2</sub>-nCB) (1) to  $f(S_1 \leftrightarrow S_0) = 0.0536$  for Ag(dbp)(P<sub>2</sub>-nCB) (4), as calculated for the T<sub>1</sub> state optimized geometries. This parameter governs the radiative TADF decay time ( $\tau^r$ ) at ambient temperature, found to be  $\tau^r = 5.6 \ \mu s$  for  $Ag(phen)(P_2-nCB)$  (1) but only  $\tau^r = 1.4 \ \mu s$  for  $Ag(dbp)(P_2-nCB)$  (4)—a record TADF value. In parallel, the photoluminescence quantum yield ( $\Phi_{PL}$ ) measured for powder samples at ambient temperature is boosted up from  $\Phi_{PL}$  = 36% for Ag(phen)(P<sub>2</sub>-nCB) (1) to  $\Phi_{PL}$  = 100% for Ag(dbp)(P<sub>2</sub>-nCB) (4). This is a consequence of a cooperative effect of both decreasing the nonradiative decay rate and increasing the radiative decay rate in the series from Ag(phen)( $P_2$ -nCB) (1), Ag(idmp)( $P_2$ -nCB) (2), and Ag(dmp)( $P_2$ -nCB) (3) to Ag(dbp)( $P_2$ -nCB) (4). Another parameter important for the TADF behavior is the activation energy of the S<sub>1</sub> state from the state T<sub>1</sub>,  $\Delta E(S_1-T_1)$ . Experimentally it is determined for the complexes Ag(dmp)(P<sub>2</sub>-nCB) (3) and Ag(dbp)(P<sub>2</sub>-nCB) (4) to be of moderate size of  $\Delta E(S_1-T_1) = 650 \text{ cm}^{-1}$ .

# INTRODUCTION

A material applied as an emitter in OLEDs should be able to harvest and convert all singlet and triplet excitons formed into light.<sup>1</sup> There are two main classes of compounds that meet this requirement. The first class is represented by complexes of heavy transition metals, which harvest all the excitons in the lowest triplet state (T<sub>1</sub>) and emit via a phosphorescence pathway, according to the *triplet harvesting mechanism*.<sup>2–6</sup> This mechanism can be realized due to heavy-metal-induced strong spin—orbit coupling (SOC), which provides fast intersystem crossing (ISC) from the singlet state to the triplet manifold and opens the spin-forbidden pathways of the T<sub>1</sub>  $\rightarrow$  S<sub>0</sub> transitions (phosphorescence).<sup>2,5</sup> The second class is represented by

compounds exhibiting thermally activated delayed fluorescence (TADF). In TADF compounds the energy of all the excitons is emitted via the lowest excited singlet state (S<sub>1</sub>); hence, the mechanism is called the *singlet harvesting mechanism*.<sup>7–12</sup> This mechanism is based on a fast thermal equilibration between the singlet and the triplet state and is related to fast down- and up-ISC (up-ISC is also called RISC) processes. The efficiency of  $T_1 \rightarrow S_1$  up-ISC strongly depends on the activation energy that can be approximated to the energy gap between the states,  $\Delta E(S_1-T_1)$ . Therefore, a small  $\Delta E(S_1-T_1)$  value or at least a

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Figure 1. Structural formulas of the investigated Ag(I) complexes.

Scheme 1. Synthetic Route to the Studied Ag(I) Complexes



moderately small value is of high importance for a compound to exhibit efficient TADF. A small energy gap  $\Delta E(S_1-T_1)$ requires a small exchange interaction between the unpaired electrons, which can be achieved when these electrons are spatially well separated.<sup>13–15</sup> This condition can be realized when the lowest excited states ( $S_1$  and  $T_1$ ) are of charge transfer character. For instance, complexes of Cu(I) with metal to ligand charge transfer (MLCT) or halide (X) and metal to ligand charge transfer (XMLCT) character of the lowest excited states often show TADF.<sup>8–10,16–35</sup> Moreover, also pure organic compounds with charge transfer character of the lowest excited states exhibit TADF behavior and can be applied in OLEDs, giving up to 100% internal efficiency.<sup>11,36–41</sup>

Interestingly, although there are numerous examples of Cu(I) complexes exhibiting TADF, analogous Ag(I) complexes rarely follow this trend.<sup>25,42-44</sup> Frequently, they exhibit longlived phosphorescence from ligand-centered (LC) excited states of  ${}^{3}\pi\pi^{*}$  character.<sup>45–48</sup> This behavior is explained by the higher ionization potential of Ag<sup>+</sup> (second ionization potential of the silver atom) in comparison to that of Cu<sup>+</sup> because of the greater atomic number of silver.<sup>49</sup> This results in more stabilized d orbitals of Ag(I) complexes. Thus, these are not involved in transitions that lead to the lowest excited states. Therefore, for a complex of Ag(I) to show TADF, the d orbitals should be destabilized and highly contribute to the frontier occupied orbitals (HOMO, HOMO-1, and HOMO-2) of the complex. This can be fulfilled using ligands of highly electron donating character, such as phosphines, and the situation is better if they carry a negative charge, which along with enhancing the electron-donating properties would additionally make the complex electroneutral.

Although an appropriate electronic structure is essential for a compound to show TADF, it is not enough for a material to be used as an efficient TADF material for OLED devices. High quantum yield of emission and short decay time are also required. It is well-known that emission quantum yields strongly depend on the molecular rigidity of the compound.<sup>19,50</sup> In particular, extensive flattening distortions in the excited states of charge transfer character as shown for

Cu(I) compounds<sup>50–59</sup> are also expected to occur in analogous Ag(I) complexes. Such distortions increase the nonradiative relaxation rate  $(k^{nr})$  of the excited state due to the increased vibrational overlap of excited state and ground state vibrational wave functions, having the consequence of reducing the emission quantum yield.<sup>19,50,56,60</sup> Therefore, in the design of TADF materials it is important to make the molecular structures rigid, along with fulfilling the electronic requirements discussed above. Having these in mind (structural rigidity, high transition rate  $k^{r}(S_1 \rightarrow S_0)$ , and small  $\Delta E(S_1 - T_1)$ ), we synthesized and investigated a series of Ag(I) complexes, namely  $Ag(phen)(P_2-nCB)$  (1),  $Ag(idmp)(P_2-nCB)$  (2),  $Ag(dmp)(P_2-nCB)$  (3), and  $Ag(dbp)(P_2-nCB)$  (4) (Figure 1) with  $P_2$ -nCB = negatively charged 1,2-bis-(diphenylphosphine)-nido-carborane ligand,<sup>61</sup> phen = 1,10phenanthroline, idmp = 4,7-dimethyl-1,10-phenanthroline, dmp = 1,9-dimethyl-1,10-phenanthroline, and dbp = 2,9-di-n-butyl-1,10-phenanthroline. All of these complexes are electroneutral and share a similar structure motif, which comprises a negatively charged P2-nCB ligand and a 1,10-phenanthrolinebased ligand coordinated to a silver cation (Figure 1).

The variation of the energy gap,  $\Delta E(S_1-T_1)$ , in the series of complexes seems to be moderate, as the experimentally obtained values for **3** and **4** are about 650 cm<sup>-1</sup>. However, the change in oscillator strength,  $f(S_1 \rightarrow S_0)$ , in the series is significant. This shows, how the TADF properties can be strongly modulated by, at first sight, very insignificant structural changes. In particular, the complex with the most advanced TADF properties, Ag(dbp)(P<sub>2</sub>-nCB) (4), exhibits an outstandingly short TADF decay time of  $\tau = 1.4 \ \mu s$  and photoluminescence quantum yield reaching unity, as measured for a powder sample under ambient conditions.

## SYNTHESIS AND STRUCTURES

A series of Ag(I) complexes was synthesized in two steps according to a procedure reported earlier.<sup>42,61-63</sup> In the first step, silver hexafluorophosphate (AgPF<sub>6</sub>) or silver tetrafluoroborate (AgBF4) was stirred in ethanol with *o*-carboranebis(diphenylphosphine) (P<sub>2</sub>-oCB) prepared in advance.<sup>42,64</sup> In



 $Ag(phen)(P_2-nCB) 1$   $Ag(idmp)(P_2-nCB) 2$ 

Ag(dmp)(P<sub>2</sub>-nCB) 3

Ag(dbp)(P2-nCB) 4

Article

Figure 2. Perspective views (OLEX-2<sup>65</sup> plots with 50% probability thermal ellipsoids) of the newly synthesized complexes. Hydrogen atoms are omitted for clarity.



Figure 3. Coordination core geometries of complexes Ag(phen)(P<sub>2</sub>-nCB) (1), Ag(idmp)(P<sub>2</sub>-nCB) (2), Ag(dmp)(P<sub>2</sub>-nCB) (3), and Ag(dbp)(P<sub>2</sub>-nCB) (4)<sup>42</sup> as found by single-crystal X-ray diffraction analysis. The given interplanar angles characterize the deviations from the tetrahedral geometry ( $\varphi = 90^{\circ}$ ) (not to be confused with the valence angle of  $109^{\circ}$  in a tetrahedral molecule such as methane).

the second step, the phenanthroline-based ligand is added to the mixture, which then was stirred under reflux conditions for 1 h. The variety of the phenanthrolines used in the second step was represented by 1,10-phenanthroline (phen), 4,7-dimethyl-1,10-phenanthroline (idmp), 2,9-dimethyl-1,10-phenanthroline (dmp), and 2,9-di-n-butyl-1,10-phenanthroline (dbp). Importantly, refluxing ethanol is a necessary reaction condition at the second step for *o*-carboranebis(diphenylphosphine) to undergo partial deboration and transform to the negatively charged nidocarboranebis(diphenylphosphine) (P2-nCB) ligand, which finally makes the obtained complexes electroneutral.<sup>62,63</sup> According to the variety of ligands with a 1,10-phenanthroline core, the complexes  $Ag(phen)(P_2-nCB)$  (1),  $Ag(idmp)(P_2-nCB)$ nCB) (2), and Ag(dmp)( $P_2$ -nCB) (3) were obtained (Scheme 1).  $Ag(dbp)(P_2-nCB)$  (4) was synthesized analogously and was reported earlier, along with its characterization.<sup>42</sup> The obtained complexes are stable in air under day light and ambient conditions. Samples under photophysical investigation did not show any sign of decomposition in 48 h. Synthetic procedures to give o-carborane-bis(diphenylphosphine) and the newly obtained complexes and structural characterizations of the compounds are given in the Supporting Information.

Single crystals for X-ray analysis were grown from  $\rm CH_2\rm Cl_2$  (DCM) solutions by slow solvent evaporation.

X-ray diffraction analyses of the obtained crystals revealed molecular structures of complexes 1–4 (Figure 2) with mean bond lengths of Ag–P and Ag–N of 2.44 and 2.31 Å, respectively, being unremarkable in comparison to Ag(I) complexes reported earlier.<sup>47,49,61,66–68</sup> In fact, the structural data obtained for Ag(phen)(P<sub>2</sub>-nCB) (1) agree very well with the data reported earlier by Crespo et al.<sup>61</sup> The structural data characterizing the coordination centers of the studied complexes are summarized in Table S2 in the Supporting Information.

It is noted that in  $Ag(dmp)(P_2-nCB)$  (3) the steric interaction of the  $P_2-nCB$  ligand with alkyl substituents of the dmp ligand, similar to the case for  $Ag(dbp)(P_2-nCB)$  (4),<sup>42</sup> stabilizes the coordination center at a geometry closer to a tetrahedron, in comparison to the complexes  $Ag(phen)(P_2$ nCB) (1)<sup>61</sup> and  $Ag(idmp)(P_2-nCB)$  (2). The significantly weaker steric interaction involving H atoms instead of the alkyl substituents in the 2- and 9-positions of phenanthroline in both  $Ag(idmp)(P_2-nCB)$  (2) and  $Ag(phen)(P_2-nCB)$  (1) results in a more flexible geometry at the coordination center. Consequently, the latter two complexes show geometries strongly deviating from that of a tetrahedron. This effect can be clearly seen from comparison of angles between planes drawn through N-Ag-N and P-Ag-P atoms (Figure 3).

It will be shown below that these structural properties and the related structural flexibility, as concluded on the basis of Xray geometries and voids around the coordination centers, can notably affect the TADF behavior. In particular, according to TDDFT calculations, the positions of the ligands relative to the coordination center correlate with the oscillator strengths of the  $S_1 \leftrightarrow S_0$  transitions, being one of the primary parameters for the TADF efficiency.

# TADF DECAY TIMES AND CRUCIAL PARAMETERS

Before investigating photophysical properties of the complexes presented above, we briefly discuss the key points important for TADF characteristics, such as emission decay time and quantum yield. The occurrence of TADF is due to efficient down- and up-ISC between the singlet and triplet states. In complexes of Cu(I) exhibiting TADF the processes of down-



**Figure 4.** Coordination core geometries of the complexes  $Ag(phen)(P_2-nCB)$  (1),  $Ag(idmp)(P_2-nCB)$  (2),  $Ag(dmp)(P_2-nCB)$  (3), and  $Ag(dbp)(P_2-nCB)$  (4) taken from the structures optimized (M06/def2-SVP, gas phase) in the electronic ground state (S<sub>0</sub>) and in the lowest excited triplet state (T<sub>1</sub>) for comparison. The interplanar angles between the P–Ag–P (orange) and N–Ag–N (blue) planes are marked.

ISC are very fast<sup>52,53,55,56,69–71</sup> (several picoseconds). A similar behavior is expected to occur for Ag(I) complexes. Fast ISC processes lead to a fast equilibration between the singlet and triplet manifolds, usually represented by the S<sub>1</sub> and T<sub>1</sub> states. Consequently, monoexponential decay of the emission can occur. It is important that the process of T<sub>1</sub>  $\rightarrow$  S<sub>1</sub> up-ISC, unlike S<sub>1</sub>  $\rightarrow$  T<sub>1</sub> down-ISC, entails thermal activation from the T<sub>1</sub> state to a vibrational state that is isoenergetic with a vibrational state of the S<sub>1</sub> state. Therefore, the efficiency of T<sub>1</sub>  $\rightarrow$  S<sub>1</sub> up-ISC, apart from SOC, depends on the energy gap  $\Delta E(S_1-T_1)$ . Accordingly, a smaller  $\Delta E(S_1-T_1)$  value favors a higher T<sub>1</sub>  $\rightarrow$  S<sub>1</sub> up-ISC rate at a given temperature. This dependence is explicitly reflected in eq 1, defining the emission decay time from equilibrated T<sub>1</sub> and S<sub>1</sub> states at a given temperature.

$$\tau(T) = \frac{3 + \exp\left(-\frac{\Delta E(S_{1} - T_{1})}{k_{\rm B}T}\right)}{3k(T_{1}) + k(S_{1}) \exp\left(-\frac{\Delta E(S_{1} - T_{1})}{k_{\rm B}T}\right)}$$
(1)

Herein  $\tau(T)$  is the emission decay time as a function of temperature,  $k(S_1)$  ( $k(S_1 \rightarrow S_0)$ ) and  $k(T_1)$  are the rates of the  $S_1 \rightarrow S_0$  and  $T_1 \rightarrow S_0$ , transitions, respectively,  $\Delta E(S_1-T_1)$  is the energy gap between the equilibrated emitting states  $S_1$  and  $T_1$ ,  $k_B$  is the Boltzmann constant, and T is the temperature. Thus, according to eq 1 the population of the  $S_1$  state from the  $T_1$  state depends exponentially on the  $\Delta E(S_1-T_1)$  energy gap. Consequently, a higher TADF efficiency is expected for a smaller  $\Delta E(S_1-T_1)$  value, as was already discussed many times.<sup>5,10,11,20–22,25,31,37,43,73–75</sup> A small  $\Delta E(S_1-T_1)$  energy gap requires a small exchange interaction between the unpaired electrons in the excited states. Therefore, the TADF effect frequently occurs for molecules that exhibit low-lying states of charge transfer character.

Moreover, a high radiative rate of the  $S_1 \rightarrow S_0$  transition  $k^r(S_1)$  favors a faster depletion of the  $S_1$  state, resulting in a shorter TADF decay time. This parameter is explicitly included in eq 1 as a pre-exponential factor. A large  $k(S_1)$  value means a good overlap of the orbitals involved in the transition, such as the HOMO and LUMO. However, a good overlap of the orbitals increases the singlet-triplet splitting  $\Delta E(S_1-T_1)$ , consequently decreasing the up-ISC rate and the TADF efficiency. Correlation of the parameters  $k(S_1)$  and  $\Delta E(S_1-T_1)$ .

 $T_1$ ) was shown for a large number of TADF Cu(I) complexes.<sup>22</sup> Therefore, designing a compound with high TADF efficiency often means finding the optimal relation between the  $k(S_1)$  and  $\Delta E(S_1-T_1)$  values.

## THEORETICAL INVESTIGATIONS

In this section, we present a theoretical introduction of electronic structures and excited state characteristics of the complexes presented in this work. DFT computations were carried out using a DFT approach at the M06<sup>76</sup>/def2-SVP<sup>77</sup> level of theory for geometry optimizations and at the M062X<sup>76</sup>/def2-SVP<sup>77</sup> level for time-dependent (TD-DFT) computations, all under gas-phase conditions and utilizing the Gaussian 09<sup>78</sup> code. The calculated ground state geometries of the complexes, in particular, characteristic angles at coordination centers, are sensitive to the substituents on the phenanthroline ligand and their positions. The two alkyl groups on positions 2 and 9 of the phenanthroline ligands in the complexes  $Ag(dbp)(P_2-nCB)$  (4) and  $Ag(dmp)(P_2-nCB)$ (3) represent strongly hindering anchors, which lead to ground state geometries being closer to a tetrahedron in comparison to complexes  $Ag(idmp)(P_2-nCB)$  (2) and  $Ag(phen)(P_2-nCB)$ (1). This result agrees well with the results from X-ray analyses discussed above.

The triplet state  $(T_1)$  relaxed geometries of the presented complexes are twisted toward planarization, in comparison to the ground state geometries. Similar structural changes in the excited state were also reported for Cu(I) complexes with charge transfer character of the lowest excited states.<sup>50–56,59</sup> This effect is more pronounced for the complexes Ag(phen)-(P<sub>2</sub>-nCB) (1) and Ag(idmp)(P<sub>2</sub>-nCB) (2) with more flexible molecular geometries than for the relatively rigid Ag(dmp)(P<sub>2</sub>nCB) (3) and Ag(dbp)(P<sub>2</sub>-nCB) (4) complexes (Figure 4 and Tables S3 and S4 in the Supporting Information).

Thus, as calculated for gas-phase conditions, the change of angle between P–Ag–P and N–Ag–N planes ( $\Delta \varphi$ ) from the ground state to the T<sub>1</sub> state is significantly larger in complexes 1 ( $\Delta \varphi \approx 34.7^{\circ}$ ) and 2 ( $\Delta \varphi \approx 34.3^{\circ}$ ) than in complexes 3 ( $\Delta \varphi \approx 8.4^{\circ}$ ) and 4 ( $\Delta \varphi \approx 11.8^{\circ}$ ). This result agrees well with the conclusion drawn on the basis of structures obtained by X-ray analyses showing that complexes 1 and 2 have more flexible molecular structures in comparison to 3 and 4. Such structural flexibility and extensive reorganizations in the emitting state

lead to strong vibrational overlap of excited state and ground state vibrational wavefunctions. This favors non-radiative relaxation and decreasing emission quantum yield.<sup>60</sup> Therefore, a strong structural reorganization of an emitter molecule between ground and emitting states is an undesired effect and should be suppressed. Indeed, complexes 3 and 4 with more rigid structures show significantly higher TADF quantum yields than the less rigid complexes 1 and 2, as shown below. For completeness, it is remarked that the angle change between P–Ag–P and N–Ag–N planes does not represent the total structural reorganization. It is only one of the reorganization parameters.

Further discussions of the electronic structures of the complexes are based on the  $T_1$  state relaxed geometries, since we want to focus on the emission properties of the complexes. It is instructive to present at first TDDFT calculations for the Ag(dmp)(P<sub>2</sub>-nCB) (3) complex. The S<sub>1</sub> and  $T_1$  states result by 96% and 94% from the HOMO  $\rightarrow$  LUMO electronic transition, respectively. An analysis of the frontier orbitals shows that the HOMO is mainly localized on the phosphines and the silver atom, whereas the LUMO is localized on the dmp ligand (Figure 5). Accordingly, the states S<sub>1</sub> and T<sub>1</sub> of



Figure 5. Isosurface (isovalue = 0.05) contour plots of the frontier molecular orbitals of Ag(dmp)( $P_2$ -nCB) (3) calculated at M062X/ def2-SVP theory level in the T<sub>1</sub> state geometry optimized at M06/ def2-SVP level under gas-phase conditions. Hydrogens are omitted for clarity.

Ag(dmp)(P<sub>2</sub>-nCB) feature metal (M) + ligand (L) to ligand (L') charge transfer (MLL'CT) character. The unpaired electrons giving the states S<sub>1</sub> and T<sub>1</sub> of extensive charge transfer character are supposed to exhibit a relatively small exchange interaction, resulting in a small energy splitting  $\Delta E(S_1-T_1)$ , which is a key factor for the occurrence of TADF. From the TD-DFT energies of vertical transitions S<sub>0</sub>  $\rightarrow$  S<sub>1</sub> and S<sub>0</sub>  $\rightarrow$  T<sub>1</sub> a splitting of  $\Delta E(S_1-T_1) = 1070 \text{ cm}^{-1}$  can be roughly estimated (for gas-phase calculations). This agrees fairly well with the experimental activation energy of  $\Delta E(S_1-T_1) = 650 \text{ cm}^{-1}$  (see Photophysical Case Study of Ag(dmp)(P2-nCB) (3)).

Interestingly, the calculated oscillator strengths f of the  $S_1 \rightarrow S_0$  transitions of the complexes Ag(phen)(P<sub>2</sub>-nCB) (1) (f = 0.0258) and Ag(idmp)(P<sub>2</sub>-nCB) (2) (f = 0.0270) deviate notably from those of Ag(dmp)(P<sub>2</sub>-nCB) (3) (f = 0.0423) and Ag(dbp)(P<sub>2</sub>-nCB) (4) (f = 0.0536). These differences are related to the geometries of the complexes. For the former complexes the ligands are more twisted toward planarization in comparison to the latter complexes (Figure 4). To verify this correlation, we imposed the calculated T<sub>1</sub> state geometry of Ag(dmp)(P<sub>2</sub>-nCB) (3) on Ag(phen)(P<sub>2</sub>-nCB) (1) and

conducted a TDDFT calculation. For this model system, we obtained an  $S_1 \rightarrow S_0$  transition oscillator strength of f = 0.0480. This is almost twice the value calculated for  $Ag(phen)(P_2-nCB)$ (1) in its own relaxed  $T_1$  state geometry (f = 0.0258) and is very close to the value obtained for Ag(dmp)( $P_2$ -nCB) (3) (f = 0.0423). A similar test, run with the  $T_1$  state geometry of  $Ag(dbp)(P_2-nCB)$  (4) imposed on  $Ag(phen)(P_2-nCB)$  (1) gives an oscillator strength for the  $S_1 \rightarrow S_0$  transition of f =0.0687. This value is even higher than that calculated for the complex Ag(dbp)( $P_2$ -nCB) (4) with f = 0.0536. These theoretical findings indicate that electronic structures and transition rates are significantly modified even by slight geometry reorganizations. Among the studied complexes the  $T_1$  state geometry of Ag(dbp)( $P_2$ -nCB) (4) shows the highest oscillator strength of the  $S_0 \leftrightarrow S_1$  electronic transitions. In fact, the variation of the oscillator strengths  $f(S_1 \rightarrow S_0)$ , calculated for the T<sub>1</sub> state geometries, is consistent with the variation found for the corresponding radiative rates as well as for the radiative TADF decay times (see Photophysical Comparison of the Investigated Ag(I) Complexes, Table 1).

### PHOTOPHYSICAL COMPARISON OF THE INVESTIGATED Ag(I) COMPLEXES

The absorption spectra of  $Ag(phen)(P_2-nCB)$  (1), Ag(idmp)- $(P_2-nCB)$  (2), Ag(dmp) $(P_2-nCB)$  (3), and Ag(dbp) $(P_2-nCB)$ (4) are similar (Figure 6). Each of the absorption spectra shows two structured intense bands between 230 and 270 nm that are assigned to  $\pi \to \pi^*$  transitions within the phenanthroline ligand and an unstructured broad band near 385/400 nm of lower absorptivity that is assigned to MLL'CT transitions according to the calculations presented in Theoretical Investigations and in analogy to heteroleptic Cu(I) complexes.<sup>24,34,79-84</sup> It is noted that the maximum of the charge transfer absorption band of  $Ag(phen)(P_2-nCB)$  (1) appears at  $\lambda_{\rm max}$  = 400 nm, whereas the analogous bands of the complexes  $Ag(dmp)(P_2-nCB)$  (3),  $Ag(idmp)(P_2-nCB)$  (2), and Ag(dbp)-(P<sub>2</sub>-nCB) (4) are blue-shifted, being found at  $\lambda_{max} = 385$  nm (Figure 6). This blue shift is caused by electron-donating effects from the alkyl substituents that increase the energies of the  $\pi^*$ orbitals (LUMO, LUMO+1) and consequently the HOMO-LUMO energy gaps.

All of the discussed complexes feature emission spectra of broad and unstructured shape. This is characteristic for emission from states of charge transfer character with a geometry distorted from that of the ground state, as in such a situation a large number of Franck–Condon (vibronic) transitions are involved in the emission process.

The emissive properties of the studied complexes show the characteristic TADF behavior. In particular, the radiative rates, determined according to  $k^{\rm r} = \Phi_{\rm PL}/\tau$ , increase by about 3 orders of magnitude upon a temperature increase from 77 to 300 K (Table 1). For example, the radiative rate of Ag(dmp)(P<sub>2</sub>-nCB) (3) increases from  $k^{\rm r}(77 \text{ K}) = 8.5 \times 10^2 \text{ s}^{-1}$  to  $k^{\rm r}(300 \text{ K}) = 2.8 \times 10^5 \text{ s}^{-1}$ . At low temperatures (T < 70 K), the complexes show  $T_1 \rightarrow S_0$  phosphorescence with decay times of several hundred microseconds up to about 1.6 ms (Table 1). Similar decay times of the phosphorescence were also reported for other Ag(I) and Cu(I) complexes.<sup>17,21,22,44,57,73</sup> With a temperature increase to ambient temperature the S<sub>1</sub> state is effectively populated from the T<sub>1</sub> state via up-ISC processes. Accordingly, an additional, very effective radiative decay path is opened representing the S<sub>1</sub>  $\rightarrow$  S<sub>0</sub> TADF process. This shortens the radiative decay time drastically. In addition, the change of

#### Table 1. Photophysical Data of Complexes 1-4 in Different Environments and at Different Temperatures

	Ph P		Ph P		Ph P		Ph $Ph$ $Ph$ $Ph$ $Ph$ $Ph$ $Ph$ $Ph$	
	Ag(pnen)(P <sub>2</sub> -nCB) 1		Ag(idmp)( $P_2$ -nCB) 2		Ag(dmp)(P <sub>2</sub> -nCB) 3		Ag(dbp)(P <sub>2</sub> -nCB) 4	
) (200 K)								
Λ <sub>max</sub> (300 K)	575 nm	577 nm	562 nm	565 nm	537 nm	540 nm	526 nm	535 nm
Ф <sub>РL</sub> (300 К)	36 %	26 %	45 %	38 %	78 %	75 %	100 %	85 %
τ(300 K)	2.0 µs		1.7 μs		2.8 µs		1.4 µs	
k <sup>r</sup> (300 K)	1.8·10 <sup>5</sup> s <sup>−1</sup>		2.6·10 <sup>5</sup> s <sup>−1</sup>		2.8·10 <sup>5</sup> s <sup>−1</sup>		7.1·10 <sup>5</sup> s <sup>−1</sup>	
k <sup>nr</sup> (300 K)	3.2·10 <sup>5</sup> s <sup>−1</sup>		$3.2 \cdot 10^5 \text{ s}^{-1}$		7.9·10 <sup>4</sup> s <sup>−1</sup>		< 2.1·10 <sup>4</sup> s <sup>-1 c</sup>	
Φ <sub>PL</sub> (77 K)	15 %		20 %		68 %		87 %	
τ(77 K)	270 µs		310 µs		804 µs		1300 µs	
k <sup>r</sup> (77 K)	$5.6 \cdot 10^2 \text{ s}^{-1}$		$6.5 \cdot 10^2 \text{ s}^{-1}$		$8.5 \cdot 10^2 \text{ s}^{-1}$		$6.7 \cdot 10^2 \text{ s}^{-1}$	
k <sup>nr</sup> (77 K)	3.1·10 <sup>3</sup> s <sup>−1</sup>		2.6·10 <sup>3</sup> s <sup>-1</sup>		$3.9 \cdot 10^2 \text{ s}^{-1}$		$1 \cdot 10^2 \text{ s}^{-1}$	
τ(T <sub>1</sub> , 40 K)			475 µs		885 µs		1570 µs	
$k^r(S_1 {\rightarrow} S_0)^a$					2.8·10 <sup>7</sup> s <sup>−1</sup>		5.6·10 <sup>7</sup> s <sup>−1</sup>	
$\Delta E(S_1 - T_1)^a$					650 cm <sup>-1</sup>		650 cm <sup>-1</sup>	
$f(S_1 \rightarrow S_0)^b$	0.0258		0.0270		0.0423		0.0536	

<sup>a</sup>Determined from the fit of experimental luminescence decay times according to eq 1, measured for a powder sample at different temperatures. <sup>b</sup>TD-DFT calculated (M062X/def2-SVP) oscillator strength based on gas-phase optimized (M06/def2-SVP) T<sub>1</sub> state geometries. <sup>c</sup>Determined assuming an error of quantum yield of 3%: i.e., assuming a value of  $\Phi_{PL} = 97\%$ .

emissive state from  $T_1$  to  $S_1$  upon temperature increase usually leads to a slight blue shift of the emission maxima as observed for all of the investigated complexes (Figure 6).

Interestingly, the emission spectra of the  $Ag(dmp)(P_2-nCB)$ (3) complex is notably blue shifted in comparison to the isoelectronic  $Ag(idmp)(P_2-nCB)$  (2) complex, although their  $S_0 \rightarrow S_1$  absorption bands are found at the same wavelength  $(\lambda_{\text{max}} = 385 \text{ nm})$ . In addition, the photoluminescence quantum yield  $(\Phi_{PL})$  of Ag(dmp)(P<sub>2</sub>-nCB) (3) at ambient temperature of  $\Phi_{PL}(300 \text{ K}) = 78\%$  is significantly higher than that of the isoelectronic Ag(idmp)(P<sub>2</sub>-nCB) (2) with  $\Phi_{PL}(300 \text{ K}) = 45\%$ , as measured for powder samples. These large differences in the emission behavior between isoelectronic complexes are related to a different extent of geometry reorganizations in the emitting state. The methyl groups on the 2,9-positions of 1,10phenanthroline leading to the dmp ligand are acting like "internal anchors", as they sterically interact with the phenyl rings of the P2-nCB ligand. This rigidifies the molecular structure of  $Ag(dmp)(P_2-nCB)$  (3) and restrains strong reorganizations in the states S1 and T1. In the case of the complex  $Ag(idmp)(P_2-nCB)$  (2) the two methyl groups at the 4,7-positions of phenanthroline giving the idmp ligand cannot act as "internal anchors" and the geometry is more flexible. This leads to energetically more stabilized excited states and thus to

red-shifted emission spectra. A higher extent of geometry reorganization in the emitting state results in larger Franck– Condon factors of vibrational ground and excited state wavefunctions and thus, leads to an increase in the nonradiative relaxation rates<sup>14,60</sup> and consequently, to a decrease of the photoluminescence quantum yield.<sup>14,50,56,60</sup> Indeed, the rate of nonradiative relaxation to the ground state, determined according to  $k^{\rm nr} = (1 - \Phi_{\rm PL})/\tau$ , increases from  $k^{\rm nr} = 7.9 \times 10^4 \, {\rm s}^{-1}$  for Ag(dmp)(P<sub>2</sub>-nCB) (3) to  $k^{\rm nr} = 3.2 \times 10^5 \, {\rm s}^{-1}$  for Ag(idmp)(P<sub>2</sub>-nCB) (2) as measured for powder samples at ambient temperature (Table 1).

Analogously considering the case of the Ag(dbp)(P<sub>2</sub>-nCB) (4) complex, the *n*-butyl groups of the dbp ligand are expected to rigidify the molecular structure to a greater extent than the methyl groups in Ag(dmp)(P<sub>2</sub>-nCB) (3) and, thus, suppress the nonradiative relaxation even more. Indeed, the Ag(dbp)(P<sub>2</sub>-nCB) (4) complex features emission spectra blue-shifted in comparison to those of Ag(dmp)(P<sub>2</sub>-nCB) (3) (Figure 6) and a higher quantum yield, reaching  $\Phi_{PL}(300 \text{ K}) = 100\%$ .

In contrast, Ag(phen)( $P_2$ -nCB) (1) exhibits the lowest quantum yield of powder samples of  $\Phi_{PL}(300 \text{ K}) = 36\%$  among the studied complexes and the most red-shifted emission spectra. This is related to the extensive geometry reorganizations in the emitting state leading to a lower energy of the  $S_1 \rightarrow$ 



Figure 6. Absorption and emission spectra of (a) Ag(phen)(P<sub>2</sub>-nCB) (1), (b) Ag(idmp)(P<sub>2</sub>-nCB) (2), (c) Ag(dmp)(P<sub>2</sub>-nCB) (3), and (d) Ag(dbp)(P<sub>2</sub>-nCB) (4). The absorption spectra are measured for dichloromethane (DCM) solutions of  $c \approx 10^{-5}$  M concentration at 300 K (black lines). The emission spectra, measured under different conditions, including DCM solutions of  $c \approx 10^{-5}$  M concentration, are reproduced in colored lines ( $\lambda_{exc}$  410 nm). The PMMA films were doped with ~1 wt % of a given complex.

 $S_0$  transition (Figure 6). A similar behavior is found for the complex Ag(idmp)(P<sub>2</sub>-nCB) (2). These findings on structure–photophysics dependences demonstrate the high importance of structural tuning in designing efficient TADF emitters. The luminescent properties can be changed drastically even by minor structural modifications.

The dependence of non-radiative relaxation rates on geometry reorganizations can also be tracked through a decrease in quantum yields on going from rigid powder samples to the less rigid PMMA films and further to fluid DCM solution. In fact, photoluminescence quantum yields of degassed DCM solutions of Ag(dmp)(P2-nCB) (3) and Ag(dbp)(P<sub>2</sub>-nCB) (4) are as low as  $\Phi_{PL}(300 \text{ K}) = 3\%$ . This significant drop in comparison to powder samples and to compounds doped in a PMMA film, respectively (Table 1), is accompanied by a strong red shift of the emission maxima (Figure 6). A similar dependence on the environment of  $\Phi_{\rm PL}$ values was also reported for Cu(I) complexes exhibiting TADF.  $^{9,22}$  The degassed DCM solutions of Ag(phen)(P<sub>2</sub>nCB) (1) and Ag(idmp)( $P_2$ -nCB) (2) were found to be hardly emissive with  $\Phi_{PL}(300 \text{ K}) \ll 1\%$ . It was not even possible to obtain the corresponding emission spectra. In a powder sample or a doped PMMA film the two methyl substituents of  $Ag(idmp)(P_2-nCB)$  (2) can act as "external anchors" interacting with the environment, thus diminishing reorganizations in the excited state in comparison to  $Ag(phen)(P_2-nCB)$ (1) and increasing the quantum yield. However, the rigidifying effect of these "external anchors" is apparently not as effective as "internal anchors" as designed for  $Ag(dmp)(P_2-nCB)$  (3) and  $Ag(dbp)(P_2-nCB)$  (4). In solution "external anchors" are largely useless, as the medium is not rigid. All these observations agree well with stronger geometry reorganizations

in less rigid media. Therefore, the emission of the studied complexes can be regarded as being enhanced by aggregation in the sense of AIE (aggregation induced emission). Aggregation restrains emission quenching induced by reorganization. Moreover, it is important to note that the investigated compounds do not show any concentration quenching. This is probably due to a self-trapping mechanism induced by a geometry change of the emitter in the excited state. In this situation, the resonance condition for energy transfer to neighboring molecules is no longer fulfilled.<sup>9,85–87</sup>

Interestingly, the theoretical investigations presented above predict that the radiative rate of the  $S_1 \rightarrow S_0$  emission depends on the geometry of the emitting state, which is strongly affected by the presence and positions of the alkyl substituents on the 1,10-phenanthroline ligand. According to the calculations, the radiative rate should increase in the series Ag(phen)(P<sub>2</sub>-nCB) (1) < Ag(idmp)(P<sub>2</sub>-nCB) (2) < Ag(dmp)(P<sub>2</sub>-nCB) (3) < Ag(dbp)(P<sub>2</sub>-nCB) (4). Indeed, this sequence is in agreement with the experimental values (Table 1). Thus, the increasing quantum yield in the given series is a result of two effects: (i) increase in the radiative transition rate. Both effects are related to the geometries and geometry reorganizations in the excited S<sub>1</sub> and T<sub>1</sub> states.

# PHOTOPHYSICAL CASE STUDY OF Ag(dmp)(P<sub>2</sub>-nCB) (3)

Important photophysical TADF parameters, such as  $\Delta E(S_1 - T_1)$  and  $k^r(S_1 \rightarrow S_0)$ , can be derived by fitting eq 1 to experimental decay times ( $\tau$ ). To obtain reliable fit parameters, these decay times should be measured over a large temperature



**Figure 7.** (left) Luminescence decay of Ag(dmp)(P<sub>2</sub>-nCB) (3) powder measured at different temperatures. (right) Luminescence decay time  $\tau$  plotted versus temperature. From a fit of eq 1 to the experimental  $\tau(T)$  plot with the  $\tau(T_1)$  value fixed at 885  $\mu$ s as determined for T = 40 K (plateau), one obtains the values  $k(S_1 \rightarrow S_0) = 2.8 \times 10^7 \text{ s}^{-1}$  and  $\Delta E(S_1-T_1) = 650 \text{ cm}^{-1}$ . The rate  $k(S_1 \rightarrow S_0) = 2.8 \times 10^7 \text{ s}^{-1}$  corresponds formally to the prompt fluorescence decay time of  $\tau(S_1) = 36$  ns. The measured quantum yields are  $\Phi_{PL}(77 \text{ K}) = 68\%$  and  $\Phi_{PL}(300 \text{ K}) = 78\%$ , respectively.

range from the phosphorescence-only plateau at low temperatures up to ambient temperature where TADF (S<sub>1</sub>  $\rightarrow$  S<sub>0</sub> transition) dominates. In this temperature range the emission quantum yield should not vary strongly. Accordingly, only powders of  $Ag(dbp)(P_2-nCB)$  (4) and  $Ag(dmp)(P_2-nCB)$  (3) can be investigated. Since results of such investigations on  $Ag(dbp)(P_2-nCB)$  (4) were already reported, we focus in this work on the powder sample of  $Ag(dmp)(P_2-nCB)$  (3). In the range 20 K  $\leq$  *T*  $\leq$  70 K, the photoluminescence decay time of  $Ag(dmp)(P_2-nCB)$  (3) barely changes and a plateau with an emission decay time of  $\tau$  = 885  $\mu$ s is observed. The corresponding emission is assigned to the  $T_1 \rightarrow S_0$ phosphorescence. With temperature increase to 150 K and above, the emission decay time shortens by 3 orders of magnitude due to thermal population of the higher lying singlet state S<sub>1</sub>, which exhibits a drastically higher radiative decay rate compared to the  $T_1 \rightarrow S_0$  transition. Accordingly, TADF becomes dominant. At temperatures from 150 to 300 K, the changes are not as drastic and the decay times show another plateau, the TADF  $(S_1 \rightarrow S_0)$  plateau (Figure 7).

The fit of eq 1 to the experimental emission decay times allows us to determine the energy gap between the lowest singlet  $(S_1)$  and triplet states  $(T_1)$  to be  $\Delta E(S_1-T_1) = 650$  cm<sup>-1</sup>. The same value was also reported for Ag(dbp)(P<sub>2</sub>-nCB) (4).<sup>42</sup>

The fit provides also the decay rate for the  $S_1 \rightarrow S_0$  transition to be  $k(S_1 \rightarrow S_0) = 2.8 \times 10^7 \text{ s}^{-1}$ , formally corresponding to a decay time of  $\tau(S_1) = 36$  ns (Figure 8). However, the corresponding prompt fluorescence cannot be measured directly due to fast ISC processes occurring within several picoseconds, as reported for Cu(I) complexes exhibiting TADF.<sup>53,55–57,69</sup> The  $k(S_1 \rightarrow S_0)$  rate of Ag(dmp)(P<sub>2</sub>-nCB) (3) is about half of that reported for Ag(dbp)(P<sub>2</sub>-nCB) (4)<sup>42</sup>



**Figure 8.** Photophysical properties of  $Ag(dmp)(P_2-nCB)$  (3) (powder) shown on a simplified energy diagram.

(Table 1). In agreement with the experiment, the theoretical calculations also predicted a lower rate  $k(S_1 \rightarrow S_0)$  for Ag(dmp)(P<sub>2</sub>-nCB) (3) than for Ag(dbp)(P<sub>2</sub>-nCB) (4), as reflected in the calculated oscillator strengths of  $f(S_1 \rightarrow S_0, 3) = 0.0423$  and  $f(S_1 \rightarrow S_0, 4) = 0.0536$  (see Theoretical Investigations)

For completeness, we want to comment on the relatively long phosphorescence decay time of  $\tau(T_1 \rightarrow S_0) = 885 \ \mu s$ . As the states S1 and T1 both have almost identical orbital origins with the same d orbital of Ag contributing to the HOMO, SOC between these states is negligible. The T<sub>1</sub> state can experience SOC to higher lying singlet states that result from orbitals carrying different d character.<sup>5,22,73,88–91</sup> The closest excited singlet state that exhibits a d orbital of angular momentum different from that in the HOMO is the  $S_4$  state with about 40% of HOMO-2  $\rightarrow$  LUMO character. However, the energy gap between the states  $T_1$  and  $S_4$  of  $\Delta E(S_4 - T_1) = 1.6$  eV is very large, as predicted by TD-DFT calculations. According to a perturbational approach, such a large energy denominator will allow only for weak SOC between the T<sub>1</sub> and S<sub>4</sub> states. Hence, a relatively long lived T<sub>1</sub> state results. This prediction agrees well with the experimentally found decay time of  $\tau(T_1) = 885$  $\mu$ s (plateau), as measured for a powder sample of Ag(dmp)(P<sub>2</sub>nCB) (3).

## CONCLUSIONS

A designing approach is demonstrated that allows efficient TADF emitters based on Ag(I) complexes to be obtained. The approach includes a specific choice of ligands on the basis of spatial structures and electronic properties. In particular, the negatively charged and strongly electron donating bis-(diphenylphosphine)-*nido*-carborane (P<sub>2</sub>-nCB) ligand is a necessary building block to provide contribution of Ag d orbitals to the higher occupied orbitals (HOMO, HOMO-1) and to localize the latter orbitals on one site of the complex. The other ligand, based on 1,10-phenanthroline fits well to the Ag(P<sub>2</sub>-nCB) moiety to localize the lowest unoccupied orbitals (LUMO, LUMO+1) of the complex. This combination of ligands in the investigated Ag(I) complexes allowed us to obtain S<sub>1</sub> and T<sub>1</sub> states of charge transfer character, as this is a crucial condition for TADF to occur.

However, reaching a TADF behavior of Ag(I)-based complexes is not the only advantage of the discussed design strategy. The efficiency of these complexes, given by the emission quantum yield and TADF decay time, can be "tuned" via the substituents on the phenanthroline ligand. These

substituents have a prominent effect on the electronic structures of the compounds as well as on the molecular rigidity controlling the nonradiative relaxation. In particular, comparison of photophysical properties of the studied complexes shows drastic increase of the  $\Phi_{PL}$  values with increasing rigidity in the sequence  $Ag(phen)(P_2-nCB)$  (1) <  $Ag(idmp)(P_2-nCB)$  (2) <  $Ag(dmp)(P_2-nCB)$  (3) < Ag(dbp)- $(P_2-nCB)$  (4). The other factor that is important for the TADF efficiency-by decreasing the radiative TADF decay time-is the radiative rate  $k^{r}(S_1 \rightarrow S_0)$  or the oscillator strength  $f(S_1 \rightarrow S_0)$  $S_0$ ) of the singlet  $S_1$  to the singlet  $S_0$  transition. The calculated oscillator strength increases also in the given sequence, as it depends on the coordination geometry of the complex in the emitting state. For instance, when  $Ag(phen)(P_2-nCB)$  (1) is compared with Ag(dbp)(P<sub>2</sub>-nCB) (4), the  $f(S_1 \rightarrow S_0)$  value (and similarly the  $k^{r}(S_{1} \rightarrow S_{0})$  rate) increases by more than a factor of 2 toward the latter compound and, hence, leads to a distinctly higher TADF rate (compare eq 1). As a result,  $Ag(dbp)(P_2 - nCB)$  (4), representing the highlight of the applied design strategy, shows the shortest radiative TADF decay time reported so far of only  $\tau^{r} = 1.4 \ \mu s$  at a photoluminescence quantum yield of  $\Phi_{PL}$  = 100%. In fact, Ag(dbp)(P<sub>2</sub>-nCB) (4) is the first compound with a TADF decay time that is even slightly shorter than the phosphorescence radiative decay time of  $\tau^{r} = 1.5 \ \mu s$  determined for the well-known  $Ir(ppy)_{3}$ complex.<sup>92</sup>

### ASSOCIATED CONTENT

### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b02002.

(Experimental details, synthetic procedures, characterizations of the synthesized complexes, photophysical instrumentation, X-ray data, computational details, excited state energies, dominant orbital excitations from TD-DFT calculations, contour plots of the molecular orbitals that participate in the formation of the discussed excited states, and calculated molecular orbital compositions (PDF)

Calculated geometries of the states  $S_0$  and  $T_1$  of the represented complexes (PDF)

#### Accession Codes

CCDC 1568483–1568485 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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