Photoinduced *E* to *Z* isomerization of tetraphenylethylene derivatives within organometallic supramolecular assemblies

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Isolation of *E*-1,2-bis(4-bromophenyl)-1,2-diphenyl-ethylene from the *E/Z* isomer mixture obtained by a McMurry coupling reaction and reaction of this isomer with imidazole followed by *N*-alkylation with *n*BuBr and anion exchange yielded the bisimidazolium tetraphenylethylene (TPE) derivative H₂-*E*-1(PF₆)₂. The reaction of H₂-*E*-1(PF₆)₂ with Ag₂O yielded the dinuclear metallarectangle [Ag₂(*E*-1)](PF₆)₂ where the two bis-NHC donors *E*-1 bridge two silver atoms. Irradiation of [Ag₂(*E*-1)](PF₆)₂ leads to *E/Z* isomerization of the di-NHC ligand and formation of *Z*-1 in the mononuclear complex [Ag(*Z*-1)]PF₆. Demetallation of the di-NHC ligand with NH₄Cl/NH₄PF₆ yielded bisimidazolium salt H₂-*Z*-1(PF₆)₂. The unique isomerization of the *E*-TPE derivative into its *Z*-isomer *via* metal complex formation/irradiation/demetallation cannot be achieved by irradiation of the individual imidazolium salt. The emissive properties of the TPE complexes [Ag₂(*E*-1)](PF₆)₂ and [Ag(*Z*-1)]PF₆ have been investigated.

N-heterocyclic carbene, tetraphenylethylene, photochemical isomerization, fluorescence, EZI process

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1 Introduction

Tetraphenylethylene (TPE) and its derivatives have become the most extensively studied aggregation-induced-emission (AIE) luminogens. They have found multiple applications since the introduction of the concept of AIE by Tang and co-workers [1,2]. Many TPE derivatives exhibit strong fluorescence in the solid state or as colloidal aggregates due to restricted intramolecular rotation (RIR), whereas the observation of almost no or only weak fluorescence in dilute solution is generally ascribed to the dynamic intramolecular rotation of the phenyl groups against the ethylene stator [3–5]. The radiationless relaxation of excitons by the RIR mechanism has been established by a wealth of theoretical and experimental research. In addition, TPE can also undergo

E/Z isomerization (EZI) under light irradiation or by heating (Scheme 1). Whether or not the EZI process leads to an emission reduction for TPE derivatives is still subject of discussion [6–9].

The photoinduced isomerization is difficult to observe for symmetrical TPE derivatives. Therefore, the EZI process has been studied with unsymmetrically disubstituted TPE derivatives [6–17]. Apart from being ideal candidates for the study of the EZI process, pure *E*- and *Z*-isomers of disubstituted TPE and the investigation of their properties has recently attracted interest based on the differences in their optical properties, host-guest chemistry and related features [18–28]. Disubstituted TPE derivatives are conventionally synthesized by the McMurry coupling of unsymmetrically substituted ketones. This protocol normally yields a mixture of *E*- and *Z*-isomers (Scheme 1) [29–32]. Separation of these isomers by column chromatography proved difficult owing

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Scheme 1 Synthesis of *E/Z*-TPE derivatives through the McMurry coupling reaction and *E/Z* isomerisation in solution (color online).

to the similarity in the properties of the isomers [29–33]. Increasing the difference in polarity of the isomers is the usual but not the only method to achieve separation of the isomers [9,34]. The isomerization of disubstituted TPE derivatives under ultraviolet (UV) irradiation or by thermal treatment constitutes a promising method to obtain pure *E*- and *Z*-isomers. However, the quantitative conversion of one isomer into the other one has not been realized so far [8,31,34], although the isomerization rate of the *E*- to the *Z*-isomer is lower than the reverse isomerization of the *Z*- to *E*-isomer due to the higher stability of the *E*-isomer (Scheme 1) [30,31,35]. Thus, the acquisition of pure *E*- and *Z*-isomers of disubstituted TPE derivatives remains a challenge both in terms of synthesis and separation technology.

The chemistry of metal complexes bearing N-heterocyclic carbene (NHC) ligands has rapidly evolved over the last years with interesting applications ranging across a diverse set of fields. Recently a number of studies have focused on metallosupramolecular assemblies obtained from poly-NHC ligands and their postsynthetic modifications [36–44]. The synthesis of poly-NHC- Ag^{I} assemblies from Ag_2O and poly-NHC precursors has been most extensively investigated. This protocol benefits not only from the simplicity of the synthetic procedure but also from the lability of $\text{Ag}^{\text{I}}\text{-C}_{\text{NHC}}$ bond [39], allowing the formation of the thermodynamically most stable reaction product and the transmetalation of the poly-NHC from silver to other metals [45–48].

We have demonstrated turn-on fluorescence by rigidification as an alternative to AIE in dinuclear complexes of tetra-NHC-substituted TPE of type **A** (Scheme 2, top) [49,50]. In complexes of type **A** both the RIR and the EZI mechanism for radiationless relaxation are disabled through the formation of two metallacycles involving *Z*-NHC donors. Inspired by the stability of the *Z*-arrangement of the NHC donors in **A** and the lability of the Ag-C_{NHC} bond in general, we assumed that dinuclear silver complexes of di-NHC substituted TPE derivatives in *E*-configuration might undergo the isomerization to the *Z*-complexes upon UV irradiation via the EZI process.

Scheme 2 Synthesis of $[\text{Ag}_2(\text{E-1})_2](\text{PF}_6)_2$ from $\text{H}_2\text{-E-1}(\text{PF}_6)_2$, the irradiation induced transformation to $[\text{Ag}(\text{Z-1})]\text{PF}_6$ and demetallation of $[\text{Ag}(\text{Z-1})]\text{PF}_6$ to give $\text{H}_2\text{-Z-1}(\text{PF}_6)_2$ (color online).

diation via the EZI process.

Here we describe the molecular rectangle $[\text{Ag}_2(\text{E-1})_2](\text{PF}_6)_2$ obtained from the bisimidazolium TPE salt $\text{H}_2\text{-E-1}(\text{PF}_6)_2$ and Ag_2O (Scheme 2, bottom). Upon irradiation, the dinuclear complex $[\text{Ag}_2(\text{E-1})_2](\text{PF}_6)_2$ quantitatively converts into the mononuclear complex $[\text{Ag}(\text{Z-1})]\text{PF}_6$. Demetallation of $[\text{Ag}(\text{Z-1})]\text{PF}_6$ yielded salt $\text{H}_2\text{-Z-1}(\text{PF}_6)_2$ which, to our knowledge, constitutes the first controlled quantitative transformation of *E*- to *Z*-TPE derivatives through an organometallic supramolecular assembly. In addition, the Ag^{I} complexes $[\text{Ag}_2(\text{E-1})_2](\text{PF}_6)_2$ and $[\text{Ag}(\text{Z-1})]\text{PF}_6$ exhibit AIE induced luminescence in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ solvent mixtures.

2 Results and discussion

The bisimidazolium salt $\text{H}_2\text{-E-1}(\text{PF}_6)_2$ was obtained by the copper-catalyzed coupling reaction of *E*-1,2-bis(4-bromophenyl)-1,2-diphenylethene and imidazole. The resulting bis(4-imidazolphenyl)-1,2-diphenylethene was obtained as a mixture of *E* and *Z* isomers and the latter one was removed by multiple crystallization steps [51]. A subsequent double *N*-alkylation with *n*-butylbromide gave the dibromide salt which was converted into the hexafluorophosphate salt $\text{H}_2\text{-E-1}(\text{PF}_6)_2$ by reaction with NH_4PF_6 (Scheme S1, for experimental details see the Supporting Information online).

The bisimidazolium salt $\text{H}_2\text{-E-1}(\text{PF}_6)_2$ was fully characterized by nuclear magnetic resonance (NMR) spectroscopy and high-resolution electrospray ionization (HR ESI) mass spectrometry (see the Supporting Information online).

In addition, the molecular structure of $H_2-E-1(PF_6)_2$ was established by an X-ray diffraction study (Figure S1, Supporting Information online).

Reaction of $H_2-E-1(PF_6)_2$ with an excess of Ag_2O in dry acetonitrile at 55 °C for 24 h under exclusion of light yielded complex $[Ag_2(E-1)_2](PF_6)_2$ in 70% yield (Scheme 2 and Scheme S2, see the Supporting Information online). The formation of the organometallic rectangle was confirmed by NMR and mass spectrometry. The 1H NMR spectrum of $[Ag_2(E-1)_2](PF_6)_2$ (Figure 1b) did not feature the resonance for the imidazolium H2 proton anymore, which was observed for the bisimidazolium salt at $\delta = 8.79$ ppm (Figure 1a). The $^{13}C\{^1H\}$ spectrum of $[Ag_2(E-1)_2](PF_6)_2$ featured the resonance for the C_{NHC} carbon atoms at $\delta = 181.6$ ppm (by 1H - ^{13}C heteronuclear multiple bond correlation spectroscopy in CD_3CN , Figure S12). The base peak in the HR ESI mass spectrum (positive ions) was detected at $m/z = 1513.4960$ (calcd for $[Ag_2(E-1)_2]PF_6^+ = 1513.4249$) (Figure 1c).

The absorption and emission spectra of $H_2-E-1(PF_6)_2$ and $[Ag_2(E-1)_2](PF_6)_2$ are depicted in Figure 2. The bisimidazolium salt $H_2-E-1(PF_6)_2$ and the dinuclear complex $[Ag_2(E-1)_2](PF_6)_2$ exhibit essentially identical absorption spectra (Figure 2a) except for the slightly enhanced vibration structure observed for $[Ag_2(E-1)_2](PF_6)_2$.

The emission spectra (Figure 2b) showed the expected weak emission for $H_2-E-1(PF_6)_2$ due to nonradiative decay enabled by rotation of the TPE benzene rings. After complex formation to give $[Ag_2(E-1)_2](PF_6)_2$, partial rigidification induced fluorescence enhancement [11] with a concurrent red-shift of the emission from $\lambda = 385$ nm (for $H_2-E-1(PF_6)_2$) to $\lambda = 492$ nm for $[Ag_2(E-1)_2](PF_6)_2$.

Based on the observation of the UV radiation induced EZI process in TPE derivatives (Scheme 1), we became interested in extending this isomerization to complexes obtained from suitably disubstituted TPE derivatives. Isomerization of the di-NHC ligand *E-1* in the dinuclear complex $[Ag_2(E-1)_2](PF_6)_2$ would lead to ligand *Z-1*, which due to steric reasons will form a mononuclear dicarbene chelate complex $[Ag(Z-1)]PF_6$ similarly to the previously described tetra-NHC substituted TPE derivatives in complex **A** (Scheme 2) [49]. The freely less stable *Z*-TPE derivative is then stabilized in the chelate complex. Removal of the TPE derivative from $[Ag(Z-1)]PF_6$ yields $H_2-Z-1(PF_6)_2$ (Scheme 2) and would then result in the selective transformation of the more stable *E*- into the less stable *Z*-derivative *via* a complex formation/isomerization reaction sequence.

Irradiation of complex $[Ag_2(E-1)_2](PF_6)_2$ in acetonitrile with a Philips mercury high-pressure lamp ($\lambda = 365$ nm) at ambient temperature yielded indeed the mononuclear chelate complex $[Ag(Z-1)]PF_6$. After irradiating of $[Ag_2(E-1)_2](PF_6)_2$ for 5 min, a new set of 1H NMR signals for $[Ag(Z-1)]PF_6$ emerged at $\delta = 7.46$ (H5), 7.37 (H4), 7.20–7.26 (H12–H14), 7.17 (H7), 6.97 (H8), 4.25 (H15) 1.94 (H16), 1.42 (H17) and

Figure 1 Sections of the 1H NMR spectra of (a) $H_2-E-1(PF_6)_2$ and (b) $[Ag_2(E-1)_2](PF_6)_2$; (c) ESI mass spectrum of $[Ag_2(E-1)_2](PF_6)_2$ (inset: observed, top; calculated, bottom, isotope distribution) (color online).

Figure 2 (a) UV-vis absorption and (b) fluorescence emission spectra of $H_2-E-1(PF_6)_2$ and $[Ag_2(E-1)_2](PF_6)_2$ (in CH_3CN , $c = 10^{-5}$ M, $\lambda_{exc} = 314$ nm) (color online).

0.99 (H18) ppm, while the intensity of the signals for the starting complex $[Ag_2(E-1)_2](PF_6)_2$ diminishes (Figure 3). The fraction of $[Ag(Z-1)]PF_6$ in the irradiated mixture rapidly increased to 68% over the first 20 min. Subsequently, the rate of EZI slowed down and after 55 min, no resonance for $[Ag_2(E-1)_2](PF_6)_2$ were detected anymore confirming complete transformation to $[Ag(Z-1)]PF_6$. The isomerization to give $[Ag(Z-1)]PF_6$ was also supported by mass spectrometry, showing only one intense peak at $m/z = 683.2305$ (calcd for $[Ag(Z-1)]^+ = 683.2297$) with the correct isotope distribution (Figure S20) for the compound obtained after irradiation of $[Ag_2(E-1)_2](PF_6)_2$.

Finally, the conversion of dinuclear $[Ag_2(E-1)_2](PF_6)_2$ to mononuclear $[Ag(Z-1)]PF_6$ can be monitored by the concurrent changes in the fluorescence emission spectra of the two complexes (Figure 4). With irradiation time, the intensity of the emission observed for $[Ag_2(E-1)_2](PF_6)_2$ at $\lambda = 492$ nm gradually decreases and a new red-shifted peak emerges at $\lambda = 512$ nm for complex $[Ag(Z-1)]PF_6$. The conversion rate monitored by fluorescence emission spec-

Figure 3 ^1H NMR spectra of $[\text{Ag}_2(\text{E-1})_2](\text{PF}_6)_2$ before (bottom) and during irradiation to give $[\text{Ag}(\text{Z-1})]\text{PF}_6$ (top) (color online).

Figure 4 Fluorescence emission spectra of $[\text{Ag}_2(\text{E-1})_2](\text{PF}_6)_2$ after different irradiation times (in CH_3CN , $c = 10^{-5}$ M, $\lambda_{\text{ex}} = 314$ nm) (color online).

troscopy is essentially identical to the rate observed by ^1H NMR spectroscopy (Figure 3). The fluorescence lifetimes of complexes $[\text{Ag}_2(\text{E-1})_2](\text{PF}_6)_2$ and $[\text{Ag}(\text{Z-1})]\text{PF}_6$ both in solution and the solid state have been determined. All values fall in the nanosecond range, suggesting fluorescence deactivation from the lowest singlet states (Table S3, Supporting Information online).

Single crystal of $[\text{Ag}(\text{Z-1})]\text{PF}_6$ suitable for an X-ray diffraction analysis was grown by slow diffusion of diethyl ether into a concentrated acetonitrile solution of the compound at ambient temperature. The X-ray diffraction study (Figure 5) confirmed the composition and geometry of $[\text{Ag}(\text{Z-1})]\text{PF}_6$ as concluded from NMR and mass spectrometric

Figure 5 Molecular structure of cation $[\text{Ag}(\text{Z-1})]^+$ in $[\text{Ag}(\text{Z-1})]\text{PF}_6$ (color online).

analysis. The two imidazolylidene donors attached to the TPE core are located on the same side of the olefin bond. They are linked by coordination to one silver atom to form a planar chelate ring. The C–Ag bond lengths of 2.084(7) and 2.092(7) Å and the C–Ag–C angle of 177.4(4)° fall in the typical range for silver (I) di-NHC complexes [10–12].

The Z-TPE bridged dicarbene ligand in $[\text{Ag}(\text{Z-1})]\text{PF}_6$ was liberated as the bisimidazolium salt $\text{H}_2\text{-Z-1}(\text{PF}_6)_2$ by reaction of the complex with NH_4Cl in a methanol and acetonitrile solvent mixture followed by anion exchange with NH_4PF_6 in methanol (Scheme 2). Compound $\text{H}_2\text{-Z-1}(\text{PF}_6)_2$ was characterized by multinuclear NMR spectroscopy and mass spectrometry (Figures S21–S23). The ^1H NMR spectrum exhibits the resonance for the imidazolium N–CH–N proton at $\delta = 8.81$ ppm. The base peak in the mass spectrum was

recorded at $m/z = 723.3044$ (calcd for $[\text{H}_2\text{-Z-1}]^+ 723.3046$).

Inspired by the irradiation induced conversion of $[\text{Ag}_2(\text{E-1})_2](\text{PF}_6)_2$ to $[\text{Ag}(\text{Z-1})]\text{PF}_6$, an equimolar mixture of the isomeric imidazolium salts $\text{H}_2\text{-E-1}(\text{PF}_6)_2$ and $\text{H}_2\text{-Z-1}(\text{PF}_6)_2$ was prepared from a 1:1 isomer mixture of *E/Z*-1,2-bis(4-bromophenyl)-1,2-diphenylethene and imidazole followed by *N*-alkylation (Scheme 3, for experimental details see the Supporting Information online). Irradiation of this mixture of bisimidazolium salts does not yield only one, the slightly more stable *E*-isomer (Figure S30). Instead, the composition of the mixture of isomeric salts does not change noticeable upon irradiation. In addition, irradiation of the single isomer $\text{H}_2\text{-E-1}(\text{PF}_6)_2$ leads to partial isomerization and formation of a mixture of isomeric salts $\text{H}_2\text{-E/Z-1}(\text{PF}_6)_2$ as shown by ^1H NMR spectroscopy (Figure S30).

Contrary to these observations, reaction of an equimolar mixture of the isomeric bisimidazolium salts $\text{H}_2\text{-E-1}(\text{PF}_6)_2$ and $\text{H}_2\text{-Z-1}(\text{PF}_6)_2$ with Ag_2O followed by irradiation of the formed complexes mixture of $[\text{Ag}_2(\text{E-1})_2](\text{PF}_6)_2$ and $[\text{Ag}(\text{Z-1})]\text{PF}_6$ with a mercury high-pressure lamp ($\lambda = 365$ nm) for 35 min yielded exclusively complex $[\text{Ag}(\text{Z-1})]\text{PF}_6$ (Scheme 3). This selectivity must be attributed to the stabilization of the *Z*-dicarbene ligand in complex $[\text{Ag}(\text{Z-1})]\text{PF}_6$ which thus becomes the only reaction product upon irradiation of the complex mixture. Such stabilization cannot occur in the bisimidazolium salts.

The transformation of the complex mixture $[\text{Ag}_2(\text{E-1})_2](\text{PF}_6)_2/[\text{Ag}(\text{Z-1})]\text{PF}_6$ into pure $[\text{Ag}(\text{Z-1})]\text{PF}_6$ was monitored by ^1H NMR spectroscopy. The ^1H NMR spectrum of the complex mixture (Figure 6, top) shows resonances for both $[\text{Ag}_2(\text{E-1})_2](\text{PF}_6)_2$ and $[\text{Ag}(\text{Z-1})]\text{PF}_6$. The spectrum after 35 min of irradiation only exhibits resonances for mononuclear $[\text{Ag}(\text{Z-1})]\text{PF}_6$.

Given the rigidification-induced desirable emission properties of dincular complexes of type A (Scheme 2) [12], we became interested in the emission properties of the less rigid complexes $[\text{Ag}_2(\text{E-1})_2](\text{PF}_6)_2$ and $[\text{Ag}(\text{Z-1})]\text{PF}_6$. The emission spectra of the complexes have been recorded in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ solution with varying water fractions. Apparently due to intramolecular phenyl rotation, the emission is weak for $[\text{Ag}_2(\text{E-1})_2](\text{PF}_6)_2$ in acetonitrile and does not change significantly as long as the water content is less than 60%. A sudden increase in emission intensity due to agglomeration accompanied by a blue shift of the emission maximum from 492 to 443 nm was observed when the water content was increased to 70% (Figure 7a). When the water content was further increased to 90%, the emission intensity increased approximately the 19 fold magnitude relative to the emission intensity in pure CH_3CN solution (Figure 7b) and the emission colour changed from invisible green to bright blue visible to the naked eye. The fluorescence quantum yield (Φ_F) reached 47% for the aggregated state in the $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ solvent mixture (with 90% water content) from $\Phi_F = 2\%$

Scheme 3 Irradiation of the complex mixture $[\text{Ag}_2(\text{E-1})_2](\text{PF}_6)_2/[\text{Ag}(\text{Z-1})]\text{PF}_6$ to give exclusively complex $[\text{Ag}(\text{Z-1})]\text{PF}_6$ (color online).

Figure 6 ^1H NMR spectrum of the complex mixture $[\text{Ag}_2(\text{E-1})_2](\text{PF}_6)_2/[\text{Ag}(\text{Z-1})]\text{PF}_6$ before irradiation (top) and after irradiation (bottom) (color online).

Figure 7 (a) Fluorescence emission spectra and (b) plot of maximum intensity for $[\text{Ag}_2(\text{E-1})_2](\text{PF}_6)_2$ in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ mixtures of varying H_2O content ($\lambda_{\text{ex}} = 314$ nm, $c = 10^{-5}$ M, $T = 298$ K). Inset: photographic image of a 10^{-5} M solution with water contents of 0 and 90 % upon excitation at $\lambda = 365$ nm using a UV lamp (color online).

observed for the pure CH_3CN solution (Table S9). Similarly to $[\text{Ag}_2(\text{E-1})_2](\text{PF}_6)_2$, complex $[\text{Ag}(\text{Z-1})]\text{PF}_6$ exhibited a blue

Figure 8 (a) Fluorescence spectra and (b) plot of maximum emission intensity for $[\text{Ag}(\text{Z-1})]\text{PF}_6$ in CH_3CN at different temperatures ($c = 10^{-5} \text{ M}$, $\lambda_{\text{ex}} = 314 \text{ nm}$) (color online).

shift ($\sim 19 \text{ nm}$) of the emission maximum and a significant increase in emission intensity (Φ_{F} up to 26.60%) as the water content of the acetonitrile/water solution reached 90% (Figures S47–S50 and Table S10).

Finally, the fluorescence behavior of complex $[\text{Ag}(\text{Z-1})]\text{PF}_6$ at different temperatures was investigated [52,53]. No obvious influence on the emission wavelength was observed by temperature dependent fluorescence spectroscopy (Figure 8a) aside from an approximately linear decrease in emission intensities with increasing temperatures (Figure 8b). The emission intensities recovered when the solutions were allowed to cool. Listings of all photophysical properties of complexes $[\text{Ag}_2(\text{E-1})_2](\text{PF}_6)_2$ and $[\text{Ag}(\text{Z-1})]\text{PF}_6$ are presented in the Supporting Information online.

3 Conclusions

We have demonstrated the quantitative isomerization of *E*- to *Z*-isomers of bisimidazolium substituted TPE by a light-triggered structural transformation *via* a dinuclear silver(I) molecular rectangle featuring an *E*-di-NHC bridge to a mononuclear silver(I) complex featuring a chelating *Z*-di-NHC. The *E*- to *Z*-isomerization is not possible directly with the bisimidazolium salts without their previous transformation into di-NHC complexes. The isomerization process of the complexes has been monitored by NMR and fluorescence emission spectroscopy. Significantly different fluorescence properties of the complexes bearing the *E* or *Z* di-NHC ligands have been observed. In addition, the complexes exhibit classical AIE characteristics. Our study provides a simple and efficient approach towards the controlled isomerization of *Z* to *E* disubstituted TPE derivatives through organometallic intermediates, paving the way for further studies of the EZI process in TPE derivatives.

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