Phosphorus corrole complexes: from property tuning to applications in photocatalysis and triplet–triplet annihilation upconversion†

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Efficient triplet photosensitizers are important for fundamental photochemical studies and applications such as triplet–triplet annihilation upconversion (TTA UC), photoredox catalytic organic reactions and photovoltaics. We now report a series of phosphorus corrole compounds as efficient visible light-harvesting metal-free triplet photosensitizers. While the heavy-atom-free phosphorus corroles show absorption in the visible spectral region (centered at 573 nm) and have a decent triplet state quantum yield (\(\Phi_A = 49\%\)), iodo-substitution on the corrole core induces red-shifted absorption (589 nm) and improves intersystem crossing significantly (\(\Phi_A = 67\%\)). Nanosecond transient absorption spectra confirm triplet state formation upon photoexcitation (\(\tau_T = 312\ \mu s\)) and the iodinated derivatives also display near IR phosphorescence in fluid solution at room temperature (\(\lambda_{em} = 796\ nm,\ \tau_p = 412\ \mu s\)). Both singlet oxygen (\(^1\text{O}_2\)) and superoxide radical anions (\(\text{O}_2^-\)) may be produced with the phosphorus corroles, which are competent photocatalysts for the oxidative coupling of benzylamine (the Aza Henry reaction).

Very efficient TTA UC was observed with the phosphorus corroles as triplet photosensitizers and perylene as the triplet acceptor, with upconversion quantum yields of up to \(\Phi_{UC} = 38.9\%\) (a factor of 2 was used in the equation) and a very large anti-Stokes effect of 0.5 eV.

Introduction

Energy up-conversion is a highly desirable process, as incident photons of a given energy are converted into photons with higher energy. It is important for applications in many fields including photovoltaic devices, luminescent probes for bioimaging, photocatalysis by low-energy photons, and photoinduced charge separation. When the efficiency of up-conversion is high enough, low-power up-conversion may be used to harness low-energy photons that, otherwise, would be lost in practical applications. For instance, it could be applied to solar cells to harvest the red and NIR part of the solar spectrum, which has energy lower than the band-gap of the employed photoactive material. Its applicability for bioimaging is even more intriguing, since excitation in the NIR region offers advantages of deeper depth penetration, suppressed background fluorescence and reduced phototoxicity.

One possible strategy for photon upconversion comes from harnessing sensitized triplet–triplet annihilation (TTA) photochemistry. Higher energy photons are generated from the absorption of lower energy light by an efficient triplet sensitizer through sequential, highly allowed one-photon absorption, subsequent intersystem crossing (ISC) and intermolecular triplet–triplet energy transfer (TTET) to the energy acceptor, and the population of the \(S_1\) state of the triplet acceptor by the TTA process. In essence, the energy stored in two sensitized triplet molecules is combined to produce one higher energy singlet state and a corresponding ground-state species. TTA upconversion is particularly interesting for its advantages over conventional upconversion methods where two photons require excitation with coherent light sources (lasers) of very high-power density (e.g. nonlinear optical crystals). In contrast, TTA upconversion requires only noncoherent low-power excitation and is characterized by intense absorption of excitation light as well as high upconversion quantum yields.
One challenge for the development of TTA upconversion is the limited availability of appropriate triplet photosensitizers.31 Commonly investigated typical triplet photosensitizers used for TTA upconversion include porphyrin and phthalocyanine complexes,28 phosphorescent transition metal complexes with diimine ligands,29 bromo- and iodo-organic chromophores,30 and a few heavy-metal-free triplet photosensitizers.32 It is relatively easy to study the intermolecular triplet energy transfer of phosphorescent photosensitizers, however, when the triplet sensitizer is non-phosphorescent, quenching must be measured by the variation of the lifetime of the T1 excited state of the sensitizer with the aid of time-resolved transient absorption spectroscopy.33 During the last decade, we and other groups have studied corroles chelated by metal ions such as gold and iridium as triplet photosensitizers, by taking advantage of the heavy atom effect for inducing efficient singlet-triplet interconversion (ISC).34–37 In parallel, we have also introduced corroles chelating non-redox active and much more abundant elements, such as Ga, Al, and P, wherein the non-radiative decay of the S1 state can be inhibited. ISC enhancement was encouraged by bromides or iodides,38,39 which in the corrole case are present on the corrole skeleton and hence not released to the environment.40,41 Corroles with reasonable ISC probability have been introduced for photodynamic therapy,41,42 molecular spintronics,43 energy transfer studies,44 and oxygen sensing.45 But to the best of our knowledge, corroles were rarely used for TTA upconversion,32,46 despite the easy tuning of their redox and photophysical properties and the extremely high stability regarding demetallation.

Results and discussion

Rational design of the compounds

We decided to focus our investigations on compounds composed of non-toxic and non-precious C, H, F, I, and P elements only (Scheme 1), as opposed to the intensively used Ru/Pt/Ir photosensitizers. The most prominent feature of corroles, particularly meso-C6F5-substituted derivatives, is strong fluorescence. As this testifies for very little non-radiative loss of energy,46 the hypothesis was that halogenation of the corrole core will increase the ISC probability and consequently the yields of the triplet excited states. Another advantage is that iodination increases red shifts of the absorbance/emission maxima and also redox potentials. The latter aspect is also tunable by the axial ligands and the number of F atoms in the meso-aryl substituents. The novelty regarding the synthetic part was to move away from hydroxo- and oxo-phosphorus corroles, which are substitution labile (converted into each other and react with solvents),47,48 to a well-defined series of substitution-inert trans-difluorophosphorus corroles, so as to allow for the systematic research described in this paper.49

Treatment of phosphorus corroles with N-iodosuccinimide (NIS) or with 1,3-diiodo-5,5-dimethylhydantoin (DIH) led to selective iodination on the corrole macrocycle (Scheme 1).44 The axial hydroxyl ligands of these iodinated complexes were exchanged with fluorides after treatment with aqueous hydrofluoric acid (Scheme 1).44 This transformation resulted in very significant and enlightening changes in the NMR spectra (Fig. S1†). The 1H resonances of hydroxyl groups disappear and the 19F signals of fluoride ligands appear, well separated from those of C6F5 and C6H3F2 aryl groups. Another prominent feature is the J ≈ 830 Hz mutual splitting coupling constant between the axial fluorides (appear as a doublet) and phosphorus (appears as a triplet).

X-ray crystallography

Being concerned about the effect of the rather large iodo-substituents on the planarity of the complexes, the X-ray structures of 1PF2-I4 and 2PF2-I4 were obtained. Fig. 1 clearly demonstrates that the deviations of the β-pyrrole substituted moieties of 1PF2-I4 and 2PF2-I4 relative to the average mean plane of all 23 carbon atoms are quite small, in the range of 0.032–0.287 Å for 2PF2-I4 and 0.000 Å for the extremely planar 1PF2-I4. The peripheral phenyl rings are not in coplanar geometry with the corrole core, and thus the π-conjugation framework of the substituted corroles is not heavily affected by the phenyl rings.

UV-vis absorption and photoluminescence of the compounds

The UV-vis absorption spectrum of 1PF2 displays an intense absorption band at 404 nm and weaker ones in the range of 500–600 nm (Fig. 2a). The former is attributed to the higher-
energy and more allowed Soret band and the latter to lower energy and symmetry-forbidden Q bands of the corrole core. Similar absorptions were observed for 1PF$_2$-I$_4$, but red-shifted by 19 nm for the Soret band and 16 nm for the Q bands, and the absorption of the lower energy band at 589 nm is intensified as compared to that of 1PF$_2$. Intensified absorption in the red-shifted region is beneficial for the application of these heavy-metal-free photosensitizers. Similar absorption profiles were observed for 2PF$_2$, 2PF$_2$-I$_3$ and 2PF$_2$-I$_4$ (Fig. 2b).

In terms of luminescence properties, there is a significant difference between 1PF$_2$ and 1PF$_2$-I$_4$ (Fig. 3). 1PF$_2$ displays emission bands in the range of 525–700 nm in different organic solvents (DCM, CH$_3$CN, and MeOH), with significant vibrational progression (Fig. 3a). This is a typical emission feature of corroles, which is also similar to the emission of porphyrin compounds. 1PF$_2$-I$_4$ has a similar emission profile in the same solvents (Fig. 3b), but the intensity is much weaker (Fig. 3c). Instead, a new emission band at 796 nm was observed in deaerated solutions of 1PF$_2$-I$_4$ at room temperature, which was completely quenched in aerated solution (Fig. 3d), consistent with phosphorescence. No phosphorescence was observed for the non-iodinated corroles under the same conditions (Fig. S28†), consistent with previous demonstration that phosphorescence of free base corroles is only recognizable at low temperature (77 K). This observation can be attributed to the enhanced ISC in the iodinated corroles, i.e. the heavy atom effect. The photophysical parameters for the phosphorus corroles in toluene are compiled in Table 1. 1PF$_2$ and 2PF$_2$ are fluorescent with quantum yields of 10% and 13% and fluorescence lifetimes of 3.3 ns and 3.7 ns, respectively. Iodination of these complexes at the corrole macrocycle reduces the fluorescence quantum yield, but also the lifetime.

**Fig. 1** Top and side views of the single-crystal molecular structure of 1PF$_2$-I$_4$ (left) and 2PF$_2$-I$_4$ (right).

**Fig. 2** UV-vis absorption spectra of (a) 1PF$_2$ and 1PF$_2$-I$_4$; (b) 2PF$_2$, 2PF$_2$-I$_3$ and 2PF$_2$-I$_4$, c = 1.0 × 10$^{-5}$ M in toluene, 20 °C.

**Fig. 3** Emission spectra ($\lambda_{ex}$ = 410 nm, optically matched solutions were used (A = 0.454), 20 °C) of (a) 1PF$_2$ in four N$_2$ saturated solvents; (b) 1PF$_2$-I$_4$ in four N$_2$ saturated solvents; (c) 1PF$_2$ and 1PF$_2$-I$_4$ in N$_2$ saturated toluene; (d) 1PF$_2$-I$_4$ in air- and N$_2$- saturated toluene (‘+’ denotes the secondary transmission of the monochromator, due to the excitation wavelength).
Table 1 Photophysical properties of the compounds

| Compound | λabs/nm | ε | λem/nm | τL | ΦL (%) | τS (μs) | ΦS (%) |
|----------|---------|---|---------|-----|--------|---------|--------|
| 1PF2     | 404, 556, 573 | 3.31, 0.30, 0.33 | 577h, 630h | 3.3j | 10j | 312 | 49 |
| 2PF2     | 405, 557, 576 | 3.12, 0.30, 0.42 | 578h, 632h | 3.7j | 13j | 192 | 46 |
| 2PF2-I3  | 415, 570, 587 | 3.06, 0.42, 0.61 | 591h, 645h, 786 | 0.48j, 338j | 0.12j, 0.15j | 127 | 60 |
| 2PF2-I4  | 417, 570, 587 | 3.06, 0.42, 0.61 | 592h, 638h, 795 | 0.14j, 530j | 0.11j, 0.36j | 181 | 71 |

a In toluene, ε = 1.0 × 10⁻³ M. b Molar absorption coefficient × 10⁷ M⁻¹ cm⁻¹. c Emission wavelength, in toluene. d Luminescence lifetimes. e Luminescence (fluorescence and phosphorescence) quantum yields, with Ru(bpy)₃[PF₆]₂ (in deaerated CH₃CN, Φₜ = 9.5%) as in ref. 54. f Triplet life time, in deaerated toluene. g Quantum yield of singlet oxygen (¹O₂). h MB (methylene blue) was used as the standard (Φₜ = 0.57 in DCM). j Fluorescence emission wavelength. k Fluorescence lifetimes (ns). l Fluorescence quantum yields. m Phosphorescence emission wavelength. n Phosphorescence lifetimes (μs). o Phosphorescence quantum yields.

Yields and the fluorescence lifetimes dramatically, and the complexes become phosphorescent at longer wavelengths (about 800 nm) with lifetimes of several hundred microseconds (Table 1). An in-depth investigation of the fluorescence lifetimes revealed a mono-exponential decay with a lifetime of 3.3 ns for 1PF2 (Fig. 4a), corresponding to the decay of the bright S₁ state of the corrole. Interestingly, for 1PF2-I₄, a bi-exponential decay was observed for the emission at 598 nm (fluorescence, Fig. 4b). A fast component (64%) is with a lifetime of 0.065 ns, which is close to the instrument response function (IRF). A long-lived (36%) component was observed with a lifetime of 3.0 ns. We attribute the fast-decaying component to the ISC, and the relatively long-lived component is due to the presence of the activation barrier for ISC, i.e., a minor component of the excited molecules does not undergo ISC. This is consistent with the low-intensity fluorescence emission seen in Fig. 3c. In other words, there is a non-university transition probability for ISC. Similar phenomena are also very often observed for molecular systems used for photo-induced electron transfer. The decay at 795 nm was also monitored and its lifetime was determined as 412 μs (Fig. 4c). Considering the large Stokes shift, the long lifetime, and the sensitivity of this emission band to O₂, the emission at 795 nm is assigned to the phosphorescence of the iodinated corrole. Room temperature phosphorescence is rarely obtained for organic chromophores with a large π-conjugation framework, but is displayed for iodinated chromophores such as iodinated Bodipy derivatives. Multiple iodo-substitutions on the corrole framework are clearly beneficial for obtaining phosphorescence. The luminescence lifetimes of the compounds in different solvents are summarized in Table S1, which reveals that 2PF2 with iodo substituents has a fluorescence lifetime that is similar to that of 1PF2. Similar results were observed for 2PF2-I₃ and 2PF2-I₄, compared with 1PF2-I₄: all of them have fluorescence lifetimes that are 10–20 times smaller relative to their non-substituted analogs, and phosphorescence lifetimes in the range of several hundred microseconds.

As a preliminary evaluation of the ISC efficiency of the corroles, the singlet oxygen quantum yields (Φₜ) were measured. For the non-iodinated corroles 1PF2 and 2PF2, the Φₜ values are 49% and 46%, respectively. These results indicate that while ISC is quite efficient even for 1PF2 and 2PF2, upon iodination, the Φₜ increases to 60–71% (Table 1), which is clearly attributed to the heavy atom effect of the iodo-substituents.

**Figure 4** Decay traces of the luminescence of (a) 1PF2 at 577 nm (fluorescence band) in toluene; (b) 1PF2-I₄ at 598 nm (fluorescence band) in deaerated toluene; (c) 1PF2-I₄ at 795 nm (phosphorescence band) in deaerated toluene. (b) Excited with a picosecond pulsed laser for the fluorescence band (λex = 405 nm), and excited with a microsecond flash lamp for the phosphorescence peak at λex = 420 nm, c = 1.0 × 10⁻⁵ M, 20 °C.

**Table 1** Photophysical properties of the compounds

| Compound | λabs/nm | ε | λem/nm | τL | ΦL (%) | τS (μs) | ΦS (%) |
|----------|---------|---|---------|-----|--------|---------|--------|
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a In toluene, ε = 1.0 × 10⁻³ M. b Molar absorption coefficient × 10⁷ M⁻¹ cm⁻¹. c Emission wavelength, in toluene. d Luminescence lifetimes. e Luminescence (fluorescence and phosphorescence) quantum yields, with Ru(bpy)₃[PF₆]₂ (in deaerated CH₃CN, Φₜ = 9.5%) as in ref. 54. f Triplet life time, in deaerated toluene. g Quantum yield of singlet oxygen (¹O₂). h MB (methylene blue) was used as the standard (Φₜ = 0.57 in DCM). j Fluorescence emission wavelength. k Fluorescence lifetimes (ns). l Fluorescence quantum yields. m Phosphorescence emission wavelength. n Phosphorescence lifetimes (μs). o Phosphorescence quantum yields.
a significant ground state bleaching band at 405 nm was observed upon photo-excitation. However, the ground state band (GSB) at 567 nm is much weaker, apparently due to the much smaller molar extinction coefficients of the ground state absorption of the compound in this region (Fig. 2), as well as the possible superimposition of the GSB with the excited state absorption (ESA) band in this region. This effect is much more significant in the range of 350–500 nm, where the ESA band also overlaps with the GSB. The transient was determined to have a lifetime of 277 μs in deaerated solution (Fig. 5c). This was reduced by 3 orders of magnitude (266 ns) in aerated solution (Fig. S35†), thus confirming that the transient absorption is of the triplet-excited state of the corrole. It should be pointed out that the observed triplet state lifetime may be attributed to the heavy atom effect in \(1\text{PF}_2\text{-I}_4\). The triplet state lifetime was determined as 179 μs (Table 1). The shorter triplet state lifetime of \(1\text{PF}_2\text{-I}_4\) as compared to \(1\text{PF}_2\) may be attributed to the heavy atom effect in \(1\text{PF}_2\text{-I}_4\). The triplet states of other compounds were also studied with nanosecond transient absorption spectra: long-lived triplet states were observed in all cases (Fig. S33†). The ESA bands of the compounds in the region of 300–550 nm can be assigned to the transition of \(T_1\) to higher triplet states, \(i.e. T_1 \rightarrow T_n\) based on TD-DFT computations (Table S2†). Interestingly, some previously reported corroles show much shorter triplet state lifetimes. For instance, corroles with non-fluorinated phenyl rings show triplet state lifetimes in the range of 0.82–3.50 μs.\(^*\) Comparison with other heavy atom containing corroles (Br, Au, Ir, Os, and Re) discloses typical excited state life times in the range of 19–183 μs, which identifies the iodinated P corroles as among the complexes with the largest excited-state lifetimes.\(^{12,13,46,59,60}\) It should be pointed out that the strong absorption of visible light and the long-lived triplet states of these corroles are beneficial for these compounds to be used as triplet photosensitizers, because these are the desired photophysical properties for intermolecular energy- or electron-transfer (vide infra).

The spatial confinement of the triplet state wavefunction of the corroles was investigated by DFT optimization studies (Fig. 6). For both \(1\text{PF}_2\) and \(1\text{PF}_2\text{-I}_4\), the triplet state wavefunction is largely confined on the corrole \(\pi\)-conjugation framework, although it also spreads slightly to the peripheral perfluorinated phenyl moieties (Fig. 6).

Although different torsion angles between the peripheral C4F4 ring and the corrole core of the two compounds were observed, \(i.e.\) the dihedral angles are 65° and 78° for \(1\text{PF}_2\) and \(1\text{PF}_2\text{-I}_4\), respectively, the confinement of the triplet states is almost the same. These different dihedral angles may safely be attributed to the iodine substitution in \(1\text{PF}_2\text{-I}_4\), which exerts some steric hindrance on the rotation of the aryl rings. The confinement of the triplet state wavefunction of the triplet state of corroles was previously studied by time-resolved electron paramagnetic resonance (TREPR), but the confinement of the triplet state was not discussed in detail.\(^{61}\)

**Fig. 5** Nanosecond transient absorption spectra of (a) \(1\text{PF}_2\) (\(\nu_{ex} = 556\) nm) and (b) \(1\text{PF}_2\text{-I}_4\) (\(\nu_{ex} = 589\) nm); decay trace of the transients of (c) \(1\text{PF}_2\) at 410 nm and (d) \(1\text{PF}_2\text{-I}_4\) at 420 nm. Excited with a nanosecond pulsed laser. \(c = 2.5 \times 10^{-6}\) M in deaerated toluene, 20 °C.

**Fig. 6** Spin density surfaces of (a) \(1\text{PF}_2\) (calculated at the B3LYP/6-31G(d) level with Gaussian 09W) and (b) \(1\text{PF}_2\text{-I}_4\) (calculated at the B3LYP/GENECPE level with Gaussian 09W) at the optimized triplet state geometry.
Production of the corrole radical anions by reversible photoreduction

The motivation for investigating photo-driven intermolecular electron transfer between the corroles and a sacrificial electron donor (triethylamine, Et₃N) was to gain fundamental information that is relevant for potential applications of the corroles as photocatalysts. UV-vis examination upon continuous white light irradiation of an anaerobic solution of 1PF₂/Et₃N disclosed that the absorption bands at 400 nm and 567 nm decreased, whereas new absorption bands in the region of 350–450 nm and 575–650 nm appeared (Fig. 7a, the ground state difference absorption spectra). These new absorption bands may safely be attributed to the radical anion of the corroles.24 Interestingly, the photo-reduction process is reversible, clearly evident by the recovery of the pink color of the corrole solution upon alternating photoirradiation and exposure to air (Fig. 7b) i.e., 1PF₂⁻ is oxidized to the neutral form of the corroles by dioxygen in air. The process of light-induced reduction of 1PF₂ to 1PF₂⁻ and reoxidation of the latter by oxygen may in fact be repeated for several cycles without degradation of the corrole, as illustrated in Fig. 7c.

We also studied the interaction of molecular oxygen with the triplet excited state and the photo-generated radical anion of the corroles (Fig. 8): singlet oxygen (¹O₂) and superoxide radical anions (O₂⁻) are expected to be formed by the two species, respectively. Spin traps selective for ¹O₂ (2,2,6,6-tetramethyl-4-piperidone, TEMP) and O₂⁻ (5,5-dimethyl-1-pyrroline-N-oxide, DMPO) were used in combination with 1PF₂ and photo-irradiation, in the presence/absence of Et₃N. The results depicted in Fig. 8 reveal the formation of the ¹O₂ scavenged product of TEMP only when Et₃N was absent (Fig. 8a and b) and of the O₂⁻-DMPO product only when Et₃N was present (Fig. 8c and d). These studies clarify that both ¹O₂ and O₂⁻ can be produced under appropriate conditions with the phosphorus corroles.24 Similar results were obtained for 2PF₂-Et₃N and 2PF₂-I₄ (Fig. S49 and S50). The ability of these phosphorus corroles to photooxidize Et₃N is attributed to their high triplet reduction potential (Table 2) relative to the onset oxidation potential of Et₃N (0.65 V, Fig. 9). The triplet excited state reduction potential of 2PF₂ (0.52 V, Table 2) is however lower than the onset oxidation potential of Et₃N. This explains the inability of 2PF₂ to be photo-reduced by TEA in the absence of O₂ (Fig. S38†).

Phosphorus corroles as photocatalysts for redox-involving organic reactions

Encouraged by the photo- and electro-chemical properties uncovered for the phosphorus corroles, it is suggested that they might be good photocatalysts for redox-involving organic reactions. The Aza Henry reaction was selected as it is an oxidative coupling of benzylamine with itself. The literature points towards two possible mechanisms for the role of the
photocatalyst: (a) production of singlet oxygen (\(1O_2\)) that reacts with the benzylamine;\(^{44}\) (b) direct electron transfer from the amine to the photoexcited dye.\(^{65}\) Porphyrins, porphycenes, and mainly the Ru(bpy)\(_3\)[PF\(_6\)]\(_2\) (bpy = 2,2′-bipyridine) or Ir(ppy)\(_3\) complex (ppy = 2-phenylpyridine) were reported as suitable photocatalysts.\(^{66}\) However, Ru(bpy)\(_3\)[PF\(_6\)]\(_2\) has only very weak absorption in the visible spectral region, and its triplet state lifetime is quite short (1.10 \(\mu\)s in CH\(_2\)CN).\(^{76}\) These photophysical features are not optimal and precious metal complex photocatalysts are also expensive. Our results show that phosphorus corroles, free of any precious or rare elements, are efficient photocatalysts for the Aza Henry reaction (Table 3). With only 1 mol% phosphorus corrole, most of the benzylamine was converted with high selectivity to \(N\)-benzylidenecarbonylamine (67–100%), at RT and after short time visible light irradiation (1 h). No reaction took place in the absence of oxygen and 2PF\(_2\) appeared to be the best photocatalyst among the phosphorus corroles that were tested in this study, despite displaying the lowest reduction potential of its photo-excited triplet state (0.52 V). This result indicates that the photocatalytic reaction mechanism in our system may be attributed to the involvement of \(1O_2\) and not the electron transfer mechanism (Scheme 2).\(^{44}\) In fact, a comparison of the oxidation potential of benzylamine and the redox potentials of the phosphorus corroles suggests that all the phosphorus corroles tested in this study cannot photo-oxidize the amine via the electron transfer mechanism. The onset potential for oxidation of benzylamine is 1.62 V, which is much higher than the photoreduction potential of the triplet excited state and even higher than the ground state oxidation potentials of all the phosphorus corroles (Table 2). We hence propose that the oxidation of benzylamine by the phosphorus corroles as photosensitizers occurs via the singlet oxygen mechanism, which is also consistent with the superiority of 2PF\(_2\) as its photoexcited state is highest in energy.

### Triplet–triplet annihilation upconversion with the phosphorus corroles as triplet photosensitizers

Considering that the corroles are characterized by strong absorption of visible light and the long-lived triplet excited state, the compounds were tested as triplet photosensitizers.

#### Table 3 Transformation of benzylamine catalyzed by different triplet photosensitizers\(^6\)

| Entry | Photosensitizer | \(T\) [°C] | \(T\) [h] | Conv. \(\%\) | \(\Phi_{UC}\) | \(\%\) |
|-------|----------------|--------|--------|--------|--------|------|
| 1     | 1PF\(_2\)      | 20     | 1.0    | 87     | 33.6   |
| 2     | 1PF\(_2\)-I\(_4\)| 20     | 1.0    | 67     | 24.8   |
| 3     | 2PF\(_2\)      | 20     | 1.0    | 100    | 38.9   |
| 4     | 2PF\(_2\)-I\(_3\)| 20     | 1.0    | 75     | 26.4   |
| 5     | 2PF\(_2\)-I\(_4\)| 20     | 1.0    | 87     | 34.1   |
| 6     | Ru(bpy)\(_3\)[PF\(_6\)]\(_2\) | 20     | 1.0    | 100    | —      |

\(^6\) Reaction conditions: benzylamine (0.5 mmol), photosensitizers (catalyst, 0.005 mmol, 1 mol%), solvent (5 mL), under an air atmosphere, \(\lambda \geq 380\) nm (20 mW cm\(^{-2}\)), 1 h, 20 °C, in MeCN/CH\(_2\)Cl\(_2\) (5 : 1, v/v). \(^{48}\) Yield was determined by \(^1\)H NMR. The conversion of the reaction was calculated by integrating the singlet peak of the featured proton in the products at (about 4.82 ppm for –CH=N–CH\(_2\)–) and that of the corresponding proton in the starting materials (at about 3.86 ppm as the singlet for H\(_2\)N–CH\(_2\)–). \(^{48}\) Reaction was monitored by TLC. Only two spots (one point was attributed to the starting material and the other was attributed to the product) were found (except the photosensitizer), and therefore the selectivity of the photocatalysis is good. \(^{48}\) TTA upconversion quantum yield with diiodo-distyryl-bodipy as the standard (\(\Phi_T = 0.101\) in DCM). The laser power density is 70.6 mW cm\(^{-2}\). \(^{48}\) Not measured.
for TTA upconversion (Fig. 10). Nitridoosmium(vi) and oxorhenium(vi) corroles were previously reported for TTA upconversion, with SG 5 (diisobutyl 3,9-perylenedicarboxylate) as the triplet acceptor, but the upconversion quantum yields were very low: 0.16%–2.0%. Based on the triplet state energy level of the corroles (approximated as 1.56 eV, by the phosphorescence emission of 1PF2-I4), perylene was selected as the triplet acceptor and the emitter (with a T1 state energy level of 1.54 eV). For 1PF2-I4, no emission was observed upon 589 nm cw laser excitation (Fig. 10b). This is due to the weak emission of 1PF2-I4 (luminescence quantum yield: 0.27%, Table 1). In the presence of perylene, however, strong emission was observed in the range of 420–550 nm, which is the characteristic emission profile of perylene. Taking into account that the excitation wavelength is 589 nm, which is insufficient for the direct excitation of perylene, the emission is safely attributed to TTA. The upconversion quantum yield was determined as 24.8% (Table 3, note that the factor of 2 was used in the equation). Similarly, upconversion was also observed with 1PF2 as the triplet photosensitizer (Fig. 10a), but its anti-Stoke’s shift was much smaller. The visual perception of the upconversion systems is shown in Fig. 11. It is clear that the blue upconverted emission with 1PF2-I4 is more significant than that of 1PF2. The highest upconversion quantum yield was observed with 2PF2 (38.9%).

In order to study the efficient TTA upconversion capability, the upconversion intensity–excitation power relationship was investigated (Fig. S43–S47†). A linear relationship, instead of the typical quadratic relationship, was observed. This is indicative of a highly efficient TTA upconversion system, with efficient triplet–triplet-energy-transfer (TTET).

The intermolecular triplet state energy transfer between the phosphorus corrole photosensitizers and the triplet energy acceptor perylene was also studied by nanosecond transient absorption spectroscopy, focusing on the quenched triplet state lifetime in the presence of increasing amounts of perylene (Fig. 12). Analysis of the Stern–Volmer plots provides the Stern–Volmer quenching constants (KSV values), in the range of...

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**Scheme 2** Proposed reaction mechanism for the photocatalytic aerobic oxidation of benzylamine with the triplet photosensitizers 1PF2, 1PF2-I4, 2PF2, 2PF2-I3 and 2PF2-I4.
Henry reaction). Efficient triplet–triplet annihilation upconversion was observed with the phosphorus corroles as triplet photosensitizers and perylene as the triplet acceptor. The upconversion quantum yield is record high, with up to $\Phi_{\text{UC}}$ = 38.9% (a factor of 2 was used in the equation) for 2PF$_2$-I$_4$ and an anti-Stokes effect of 0.5 eV, an outcome of appropriate adjustment of excited-state lifetimes and redox potentials. This work demonstrates that phosphorus corroles can be developed as a new type of efficient triplet photosensitizers for photocatalytic organic reactions and photon up-conversions.

**Experimental**

**General methods**

All the chemicals used in synthesis were analytically pure and were received. 1P(OH)$_2$, 1PF$_2$, 2PF$_2$, 2OH$_2$-I$_3$, and 2OH$_2$-I$_4$ were synthesized as previously reported. Fluorescence quantum yields were measured in toluene, with Ru(bpy)$_3$PF$_6$ in deaerated CH$_3$CN ($\Phi_F = 9.5\%$) as in ref. 54. The molecular structures of the corroles are shown in Scheme 1. The fluorescence lifetimes of the compounds were measured with an OB920 luminescence lifetime spectrometer (in TCSPC detection mode. Edinburgh Instrument Ltd., UK). Fluorescence lifetimes were measured with 405 nm EPL picosecond pulsed laser excitation (pulse width: 51.9 ps, maximum average power: 5 mW). The phosphorescence lifetimes were measured with a $\mu$s flash lamp (maximum average power: 100 $\mu$W). Fluorescence and triplet–triplet annihilation (TTA) upconversion spectra were recorded with a RF 5301PC spectrofluorometer (Shimadzu, Japan). $^1$H and $^{19}$F NMR spectra were recorded using a Bruker Advance III 400 MHz spectrometer (operating at 400.4 MHz for $^1$H and at 376.7 MHz for $^{19}$F). Chemical shifts are reported in ppm relative to the residual hydrogen atoms in the CDCl$_3$ solvent ($\delta = 7.26$), and relative to CFCl$_3$ ($\delta = 0.00$) in the $^{19}$F NMR spectra. Mass spectra for the compounds were recorded on a Bruker MaXis Impact mass spectrometer, using an APC1 (atmospheric pressure chemical ionization) direct probe in either positive or negative mode.

**Synthesis and characterization**

**Synthesis of 2PF$_2$-I$_4$.** A sample of 2OH$_2$-I$_3$ (20 mg, 18.2 $\mu$mol) was dissolved in CH$_2$Cl$_2$ (5 mL) in a small plastic flask. 2 mL of 40% hydrofluoric acid (caution! HF should be handled with extreme care. It is a highly corrosive inorganic acid and can cause deep tissue damage) was added and the mixture was stirred overnight. The CH$_2$Cl$_2$ solution was separated and washed twice with distilled water, and the organic layer was dried over anhydrous sodium sulfate and evaporated. The purple solid material was crystallized in n-hexane/CH$_2$Cl$_2$ (1 : 1, v/v) to afford pure 2PF$_2$-I$_4$ in 92% yield (18 mg, 16.7 $\mu$mol). $^1$H NMR (400.4 MHz, CDCl$_3$; $\delta$ = 9.99 (broad s, 1H), 8.89 (broad s, 2H), 8.69 (broad s, 2H), 8.75 (unresolved m, 3H), $^1$H NMR (400.4 MHz, CDCl$_3$; $\delta$ = 9.99 (broad s, 1H), 8.89 (broad s, 2H), 8.69 (broad s, 2H), 7.75 (unresolved m, 3H), $\delta$ = 7.26, and relative to CFCl$_3$ ($\delta$ = 0.00) in the $^{19}$F NMR spectra. Mass spectra for the compounds were recorded on a Bruker MaXis Impact mass spectrometer, using an APC1 (atmospheric pressure chemical ionization) direct probe in either positive or negative mode.

**Conclusions**

A series of phosphorus corroles with peripheral fluorinated phenyl moieties were prepared, with focus on those that are also with iodo-substituents on the $\pi$-conjugation core. The photophysical properties were studied by both steady state and time-resolved spectroscopies. The corroles display intense absorption in the visible spectral region (centered at 404 nm for 1PF$_2$), and iodo-substitution on the core induces up to 19 nm red-shifts of the absorption band. Near IR phosphorescence (centered as 796 nm) was observed in fluid solution at room temperature for the iodo-substituted derivatives, whereas the regular phosphorus corroles emit only fluorescence. Transient absorption spectroscopy was used for determining photoexcited triplet state formation and lifetimes ($\tau_{T2}$), which ranged from $\tau$ = 412 to 179 $\mu$s. Singlet oxygen quantum yields ($\Phi_\Delta$) of the compounds were elucidated to be in the range of 46–71%, with higher quantum yields for the iodo-containing corroles. Properly tuned photo-excited corroles react with both reductive and oxidative quenchers, as exemplified by their reactions with a frequently used sacrificial electron donor (triethyloxiamine) and the formation of superoxide radical anions ($O_2^{-}$), respectively. They may hence be very useful as photoredox catalysts for many organic transformations. This was exemplified by utilizing the phosphorus corroles as triplet photosensitizers for efficient photocatalytic oxidative coupling of benzaldehyde (the Azato
124.50, 115.55, 114.47, 111.98, 111.79, 111.74, 101.11. UV-vis (toluene) \( \lambda_{\text{max}} (e) \text{[nm] (x \times 10^5 \text{ cm}^{-1} \text{ M}^{-1})} \): 415 (2.88), 570 (0.42), 587 (0.61). HR-MS (APCI) for \( \text{C}_{23}\text{H}_{14}\text{N}_{4}\text{F}_{13}\text{P} \cdot \text{m} \): m/z = 1077.7957 (calculated), 1077.8015 (observed).

**Synthesis of 2PF\(_2\)-I\(_4\).** The procedure for axial ligand substitution was performed on complex \( 2\text{P(OH)}_2\)-I\(_4\) by the same method and for the same amounts as for complex \( 2\text{P(OH)}_2\)-I\(_4\). 17 mg (85% yield, 16.7 \( \mu \)mol) was obtained after crystallization from \( \text{n-hexane/CDCl}_3: 1: 1 \). \(^1\)H NMR (400.4 MHz, CDCl\(_3\)) \( \delta = 8.93 \) (\( t, J = 4.8 \text{ Hz}, 2\text{H} \)), 8.71 (\( t, J = 4.8 \text{ Hz}, 2\text{H} \)), 7.75 (unresolved m, 3H), 7.30 (unresolved m, 6H). \(^31\)P NMR (376.75 MHz, CDCl\(_3\)): \( \delta = -37.52 \) (\( d, J = 832.61 \text{ Hz}, 2\text{F} \)), -108.01 (unresolved m, 4F), -108.14 (unresolved m, 2F). \(^{13}\)C NMR (128.95 MHz, CDCl\(_3\)) \( \delta = 108.14 \) (unresolved m, 2F). HR-MS (APCI) for \( \text{C}_{22}\text{H}_{14}\text{N}_{4}\text{F}_{13}\text{P} \cdot \text{m} \): m/z = 1363.601 (calculated), 1363.6018 (observed).

**X-ray quality crystals of 1PF\(_2\)-I\(_4\).** X-ray quality crystals of 1PF\(_2\)-I\(_4\) were obtained from recrystallization from a mixture of \( \text{CH}_2\text{Cl}_2: \text{n-hexane (1: 1, v/v)} \) solution. Crystal data for \( \text{C}_{23}\text{H}_{14}\text{N}_{4}\text{F}_{13}\text{P} \cdot \text{m} \): molar mass (M) = 1289.01 g mol\(^{-1}\); monoclinic, space group \( P2_1/c \) (no. 14), \( a = 21.925(2) \text{ Å, } b = 13.102(11) \text{ Å, } c = 13.146(3) \text{ Å, } \beta = 97.96(5) \text{°, } V = 3740.0(11) \text{ Å}^3 \). \( Z, T = 4, T = 200.15 \text{ K, } \mu(\text{MoK} \alpha) = 3.596 \text{ mm}^{-1} \), Deconv = 2.289 g cm\(^{-3} \), 6114 reflections measured (3.752 \( \leq \theta \leq 48.42\)°), 3932 reflections measured (4.11 \( \leq \theta \leq 48.42\)°), 3932 unique (\( R_{\text{int}} = 0.0650, R_{\text{sigma}} = 0.0384 \) which were used in all calculations. The final \( R_1 \) was 0.0569 \( (I > 2\sigma(I)) \) and \( wR_2 \) was 0.1438 (all data). CCDC 1888513.

**Synthesis of 1PF\(_2\)-I\(_4\).** A sample of \( 1\text{P(OH)}_2 \) (40 mg, 46.6 \( \mu \)mol), 50 eq. of \( \text{N-iodosuccinimide (NIS, 524 mg)}, \) and TFA (200 \( \mu \)l) were dissolved in acetonitrile (10 ml). The solution was stirred for 4 h at room temperature in the dark. The reaction mixture was diluted with \( \text{CH}_2\text{Cl}_2 (40 \text{ ml}) \), washed with distilled water (50 ml), dried over anhydrous sodium sulfate, and evaporated. The reaction products were chromatographed on silica gel by using hexanes/ethyl acetate (100: 5, v/v) as the eluent. The product was further purified by silica gel 60 preparative thin-layer chromatography (PTLC) with \( \text{n-hexane/ethyl acetate (100: 3, v/v)} \) as the eluent. The product was eluted as the third fraction with purple color (20 mg, 32% yield). \(^1\)H NMR (400.4 MHz, CDCl\(_3\)) \( \delta = 8.80 \) (dd, \( J = 4.8, 3.2 \text{ Hz}, 2\text{H} \)), 8.62 (dd, \( J = 4.8, 3.2 \text{ Hz}, 2\text{H} \)), -4.11 (d, \( J = 7.6 \text{ Hz}, 2\text{H} \)). \(^31\)P NMR (376.75 MHz, CDCl\(_3\)): \( \delta = -136.10 \) (dd, \( J = 23.0 \text{ Hz}, 7.5 \text{ Hz}, 4\text{F; ortho-F} \)), -136.35 (dd, \( J = 23.0, 7.5 \text{ Hz}, 7.5 \text{ Hz, 4F; para-F} \)), -150.68 (d, \( J = 21.1 \text{ Hz}, 2\text{F; para-F} \)), -150.94 (t, \( J = 21.5 \text{ Hz}, 2\text{F; para-F} \)), -160.48 (m, 2F, meta-F), -161.46 (m, 4F, meta-F). \(^{13}\)C NMR (128.95 MHz, CDCl\(_3\)) \( \delta = -88.00 \) (s). UV-vis (toluene) \( \lambda_{\text{max}} (e) \text{[nm] (x \times 10^5 \text{ cm}^{-1} \text{ M}^{-1})} \): 428 (2.6), 551 (0.17), 596 (0.60). HR-MS (APCI) for \( \text{C}_{19}\text{H}_{23}\text{F}_{16}\text{N}_{4}\text{P} \cdot \text{m} \): m/z = 1361.6612 (calculated), 1361.6418 (observed).

**Synthesis of 1PF\(_2\)-I\(_4\).** The procedure for axial ligand substitution was performed on complex \( 1\text{P(OH)}_2\)-I\(_4\) by the same method as for complex \( 2\text{P(OH)}_2\)-I\(_4\) and for the same amounts as for complex \( 2\text{P(OH)}_2\)-I\(_4\). 18 mg (90% yield, 13.2 \( \mu \)mol) was obtained after crystallization from \( \text{n-hexane/CDCl}_3: 1: 1 \), v/v). \(^1\)H NMR (400.4 MHz, CDCl\(_3\)) \( \delta = 8.98 \) (broad s, 2H), 8.78 (broad s, 2H). \(^{13}\)C NMR (376.75 MHz, CDCl\(_3\)): \( \delta = -27.20 \) (d, \( J = 818.19 \text{ Hz}, 2\text{F} \)), -135.72 (unresolved m, 2F; ortho-F), -136.47 (unresolved m, 4F; ortho-F), -150.41 (t, \( J = 21.80 \text{ Hz}, 1\text{F; para-F} \)), -150.92 (t, \( J = 21.80 \text{ Hz}, 2\text{F; para-F} \)), -160.75 (m, 2F, meta-F), -160.92 (m, 4F, meta-F). \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \( \delta = -183.58 \) (t, \( J = 819.1 \text{ Hz} \)). \(^{13}\)C NMR (128.95 MHz, CDCl\(_3\)) \( \delta = 139.00, 136.53, 129.05, 126.70, 126.62, 126.54, 124.15, 123.07, 100.23, 100.17, 95.92. UV-vis (toluene) \( \lambda_{\text{max}} (e) \text{[nm] (x \times 10^5 \text{ cm}^{-1} \text{ M}^{-1})} \): 423 (2.8), 544 (0.15), 589 (0.62). HR-MS (APCI) for \( \text{C}_{23}\text{H}_{14}\text{N}_{4}\text{F}_{13}\text{P} \cdot 2\text{H}_2\text{O} \cdot \text{m} \): m/z = 1363.5919 (calculated), 1363.6068 (observed).
measured in toluene. The excitation wavelength was 573 nm (A = 0.222) for 1PF₃, 576 nm (A = 0.218) for 2PF₃, and 589 nm (A = 0.203) for the other compounds. The monochromatic light source includes a xenon lamp and a monochromator. Methylene blue (MB) was used as the standard (Φₛₐₖ = 0.57 in DCM).

**Nanosecond transient absorption spectroscopy.** The nanosecond transient absorption spectra were obtained with a LP980-K Laser Flash Photolysis Spectrometer (kinetic mode, Edinburgh Instruments, UK). The analogue signal was digitized with a Tektronix TDS 3012C oscilloscope. The samples were purged with N₂ for 15 min and excited with a nanosecond pulsed laser (Opolette™). The wavelength is tunable in the range of 210–2400 nm. OPOTEK, USA. The raw data were analyzed by using LP900 software.

The general procedure for transformation of benzylamine catalyzed by different triplet photosensitizers. The mixture of photosensitizer (1 mol%) and benzylamine (0.5 mmol) in CH₃CN (5 mL) was stirred at room temperature (RT) under an air atmosphere. The solution was irradiated using a 35 W xenon lamp through a cut off filter (0.72 M NaNO₃ aqueous solution, which is transparent for light > 380 nm). Thin layer chromatography (TLC) was used to monitor the progress of the reaction. After completion of the reaction, the solvent was evaporated under reduced pressure. The conversion of the photoreactions was determined by ¹H NMR: calculated by the peak areas of the corresponding proton in the starting materials (singlet at 3.86 ppm for H₂N–CH₃) relative with that of the corresponding proton in the starting materials: (singlet at 3.86 ppm for H₂N–CH₃).

**Photoreduction of the corroles to produce radical anions.** UV-vis difference absorption spectra of the corroles were recorded in the presence of Et₃N in deaerated MeCN with white light photoradiation using a xenon lamp. Et₃N was used as the sacrificial electron donor and corrole was used as the electron acceptor. Photos were taken to show the color change using a digital camera.

**Triplet–triplet annihilation upconversion.** A 532 nm and 589 nm continuous wave (cw) diode-pumped solid state laser was used as the excitation source for the upconversion. The mixed solution of the triplet photosensitizers and the triplet acceptors was degassed with N₂ for at least 15 min before the upconversion experiments. The upconverted fluorescence was recorded with a RF 5301PC spectrofluorometer. In order to depress the laser scattering in the sample chamber of the spectrometer, a small black box was put behind the cuvette as the beam dump to trap the transmitted laser. The upconversion quantum yields (ΦUC) of the corroles in toluene were determined, relative to diiodo-distyryl-bodipy as the standard: Φᵣ = 0.101 in DCM. Plots of UC intensity vs. power density, in the range of 30–900 mW cm⁻², were linear with unity slopes (Fig. S43–S47†). The upconversion quantum yields were calculated with the following equation (eqn (2)), where Φᵣ, Α, Ι and η represent the quantum yield, absorbance, integrated photoluminescence intensity and refractive index, respectively. Symbols with ‘std’ and ‘sam’ present the corresponding parameter for the standard and sample (eqn (2)). Note a factor of 2 was used in the equation.²

$$\Phi_{UC} = 2\Phi_{std} \left( \frac{1 - 10^{-4\alpha_{std}}}{1 - 10^{-4\alpha_{sam}}} \right) \left( \frac{m_{sam}}{m_{std}} \right) \left( \frac{\eta_{sam}}{\eta_{std}} \right)^2 \tag{2}$$

**Theoretical computations.** Density Functional Theory (DFT) and Time-dependent Density Functional Theory (TD-DFT) were used for geometry optimization and energy calculation of all the compounds in a vacuum. All the calculations were performed with the Gaussian 16 program. The geometry optimization of the ground state and the excited state was conducted at the B3LYP/6-31G(d) level for non-iodo-substituted compounds and the B3LYP/GENECP level for iodo-substituted compounds and frequency calculations guarantee that the optimal structures are valid. Vertical excitation energies of singlet and triplet states were calculated at the B3LYP/6-31G(d) level for non-iodo-substituted compounds and the B3LYP/GENECP level for iodo-substituted compounds. The Gaussian 09W program package was used for the calculations.⁵

**Conflicts of interest**

There are no conflicts to declare.

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