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Intragel photoreduction of aryl halides by green-to-blue upconversion under aerobic conditions†‡

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The first proof of concept for the application of intragel green-to-blue photon upconversion to a chemical reaction is reported. The developed method allows the photoreduction of aryl halides at room temperature under aerobic conditions.

Through millions of years of evolution, nature has used confinement and compartmentalization to access otherwise slow or forbidden pathways and achieve high selectivity under mild conditions.[1] This has inspired scientists all over the world to study the effects of reactant confinement in non-conventional media on their chemical properties and reactivity.[2] The fields of photochemistry and photocatalysis, among others, have also capitalized on the benefits of spatial confinement,[3–6] which are related to changes in key properties such as light absorption, formation of redox intermediates, lifetime of excited species, thermodynamics of reacting mixtures, kinetics of competitive steps and adsorption/desorption of chemical species.[3,7,8]

Literature precedents of confined photoinduced reactions involve the use of mesoporous inorganic materials,[9] microemulsions,[10] micelles,[11] vesicles,[12] polyelectrolyte multilayered capsules,[13] proteins[14] and photocatalyst-loaded liquid foams,[15] among others.[16] Furthermore, we have recently reviewed an emerging research field focused on the use of viscoelastic gels[17] as tunable and processable reaction vessels for photochemical and photophysical transformations of embedded reactants, providing similar or superior results than those obtained in solution.[18] Among these photo-induced processes, photon up-conversion (UC)[19] based on triplet–triplet annihilation (TTA) between organic compounds is one of the most powerful wavelength conversion technologies that can be performed with low-intensity and non-coherent light.[20] TTA-UC involves the generation of the triplet

excited state (T_1) of a donor (sensitizer) by intersystem crossing (ISC) from the singlet excited state (S_1) which is formed by low energy absorption ($h\nu_1$). Subsequently, triplets of the acceptor (emitter) are populated by triplet–triplet energy transfer (TTET) from the triplets of the donor (Dexter mechanism). A higher singlet energy level is accessed upon collision of two acceptor molecules in their triplet states (TTA) causing delayed upconverted fluorescence ($h\nu_2$) (Fig. 1). Such photochemical cascade of events have found high-tech applications in several fields including photovoltaics, photocatalysis, bioimaging and phototherapy.[21–24]

The first examples of TTA-UC within gel networks using different chromophore pairs have been reported very recently by the groups of Simon,[25] Schmidt[26] and Kimizuka.[27–29] These studies demonstrated the highly efficient photochemical UC in organogel media and, in some cases, even under air-saturated conditions.[27] A major aspect of this approach is the adaptable nature of supramolecular fibrillar gel networks, which allows efficient and cooperative incorporation of donor/acceptor pairs while preserving the structural integrity of the bulk material. Such promising results prompted us to investigate applications of intragel TTA-UC to accomplish chemical transformations *via* single electron transfer (SET) that are unaffordable in solution
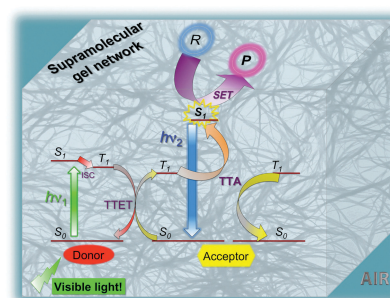

Fig. 1 General concept of this work: two photons process based on TTA-UC produces one photon of higher energy that can be used in chemical reactions. This event can be achieved using visible light at r.t. and in air when confined into a gel doped with a donor/acceptor pair. R = reactant; P = product.

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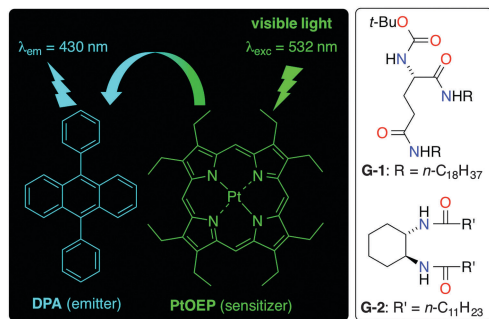
Fig. 2 Left: Illustration of green-to-blue photon UC with **PtOEP/DPA**. Right: Structures of the LMW gelators **G-1** and **G-2** used in this work. Hydrogen bonds and van der Waals forces drive their self-assembly in organic solvents producing tangled fibrillar nanostructures over a wide concentration range. Solvent-dependent critical gelation concentrations (CGC) ranged from 2–21 g L^{-1} and 2–44 g L^{-1} for **G-1** and **G-2**, respectively.[31,32]

under mild conditions (Fig. 1). As a proof of concept, we report herein the first intragel photoreduction of aryl halides by green-to-blue photon upconversion at room temperature under aerobic conditions.

For this proof of concept study we focused on the photo-reduction of aryl halides using platinum(II) octaethyl-porphyrin (**PtOEP**) as sensitizer and 9,10-diphenylanthracene (**DPA**) as emitter embedded in supramolecular (physical) gel networks (Fig. 2). The **PtOEP/DPA** system has been previously characterized and employed as a benchmark donor/acceptor pair in TTA-UC studies[24,30] including the intragel process,[27] which made it the ideal choice for our study. For comparison, we employed two well-known low molecular weight (LMW) gelators, namely *N,N′*-bis(octadecyl)-L-boc-glutamic diamide (**G-1**)[27,31] and *N,N′*-((1*S*,2*S*)-cyclohexane-1,2-diyl)didodecanamide (**G-2**),[32] to provide physical gels as confined reaction media.[33,34] On the other hand, aligned to the growing research field of visible light-mediated reactions[35] we chose the photoreduction of aryl halides as model reaction because it constitutes a major scientific challenge at visible wavelengths due to their high bond dissociation energies (BDE). This is especially critical in the case of non-activated aryl bromides whose BDE (*e.g.*, BDE$_{PhBr}$ = 3.6 eV) significantly exceeds the maximum of a single visible photon (3.1 eV).[36,37] Their reduction potentials (*e.g.*, PhBr = −2.68 eV *vs.* SCE)[38] are also beyond the excited triplet energies of common photoactive 1e-reductants (*e.g.*, [Ir(ppy)$_3$]$^+$ = 2.5 eV; [Ru(bpy)$_3$]$^{2+}$ = 2.0 eV).[39] Indeed, only few examples based on photoinduced electron transfer (PET) have been reported to achieve such bond activation.[40] However, the application of TTA-UC confined in a supramolecular microenvironment for this purpose has remained unexplored.

For initial optimizations, an aerated DMF solution of **1** (10 mM), **PtOEP** (33 μM) and **DPA** (6.7 mM) was photolyzed with a pulsed laser at 532 nm for 2 h leading to very low conversion of **1** (Table 1, entry 1). This result was attributed to chemical decomposition of the donor **PtOEP** by dissolved molecular oxygen, which rapidly diffuses into the organic medium. This was supported by nearly complete decolorization of the solution after irradiation (Fig. 3A). In sharp contrast, a remarkable increase of conversion, excellent mass balance and good overall

Table 1 Intragel photoreduction of **1** in air (ΔG$_{ET}$ = −1.8 kcal mol^{-1})^a

Entry	Gelator	[G]^k (g L^{-1})	Conversion^l (%)	Mass balance (%)	Yield^m (%)
1^b	—	—	6	96	2
2	G-1	10	65	98	58
3^c	G-1	10	0	—	0
4	G-1	6	55	93	42
5	G-1	7	53	98	47
6	G-1	8	48	99	43
7	G-1	13	59	84	40
8	G-1	20	60	88	44
9^d	G-1	10	13	100	14
10^e	G-1	10	54	99	48
11^f	G-1	10	32	93	24
12^g	G-1	10	68	93	56
13^h	G-1	10	10	98	9
14^i	G-1	10	24	97	19
15^j	G-1	20	0	—	0
16	G-2	10	60	90	47
17	G-2	15	62	89	48

^{a} Conditions (unless otherwise indicated): [**1**] = 10 mM, [**PtOEP**] = 33 μM, [**DPA**] = 6.7 mM, in air, room temperature, 2 h irradiation with a pulsed laser at λ$_{exc}$ = 532 nm. Gels were prepared using the indicated gelator in DMF. ^{b} 2 h irradiation in aerated DMF solution. ^{c} Control experiment in the absence of **PtOEP**. ^{d} [**1**] = 50 mM. ^{e} 3 h irradiation. ^{f} [**DPA**] = 1.0 mM. ^{g} Experiment under N$_2$. ^{h} 2 h irradiation using green LED (λ$_{max}$ = 525 nm, 3.8 W). ^{i} 24 h irradiation using green LED (λ$_{max}$ = 525 nm, 3.8 W). ^{j} Control experiment using benzene as solvent. ^{k} Concentration of LMW gelator. ^{l} Conversion calculated by GC/FID. ^{m} Total yield calculated by GC/FID. n-Pentadecane was used as internal standard for quantitative GC/FID analyses. Estimated error from randomly duplicated experiments ±2%. See ESI.

yield were observed when the gel made of **G-1** in aerated DMF was used as confined medium (Table 1, entry 2). No decolorization of the mixture was observed after light exposure in this case (Fig. 3B), indicating that the TTA system (**PtOEP/DPA**) was stable under these conditions affording the photoreduction product **2** without formation of byproducts. Irradiation experiments were carried out at r.t. in a climatized room; potential thermal effects were ruled out by measuring the temperature of the gel samples after 2 h irradiation, which showed an increment
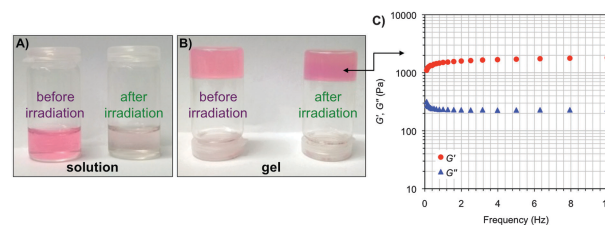

Fig. 3 (A) Photographs of doped solutions before/after irradiation (Table 1, entry 1) showing decolorization caused by degradation of **PtOEP**. (B) Photographs of doped gel before/after irradiation (Table 1, entry 2). T$_{gel}$ (48 ± 2 °C) remained constant after irradiation. (C) Dynamic frequency sweep rheological experiment (25 °C, 0.01% strain) confirming the preservation of the gel network after irradiation. tan δ = 0.165. See ESI.‡

of only 2 °C. Furthermore, oscillatory rheological measurements (*i.e.*, DFS, DSS and DTS) confirmed the preservation of the gel nature of the samples after irradiation. Destruction of the gels at low frequency and below 5% strain indicated the brittle nature of the materials. DTS measurements at 0.01% strain and 1 Hz frequency confirmed the stability of the gel materials as a function of the ageing time at room temperature. The storage modulus G' was approximately one order of magnitude higher than the loss modulus G'' within the linear viscoelastic regime (Fig. 3C). Gel-to-sol transition temperatures (T_{gel}), absolute moduli and mean values of tan δ were found almost invariable within the experimental error both after initial gel doping and after irradiation, suggesting the maintenance of the mechanical damping properties of the parent (undoped) supramolecular gel network during the experiments (Fig. S2, ESI‡).

As expected, the control experiment in the absence of the donor **PtOEP** showed no conversion (Table 1, entry 3). At this point, mixtures of **1**, **PtOEP** and **DPA** in the presence of different **G-1** concentrations were submitted to steady-state irradiations. Similar conversions as well as mass balances and total yields were obtained for all cases (Table 1, entries 4–8) suggesting that **G-1** was not involved in the photoreaction, but playing a crucial role as nanoreactor. In comparison to the result obtained under optimized conditions (Table 1, entry 2), the use of either higher substrate concentration, longer irradiation times or lower acceptor concentration resulted in lower conversions and yields (Table 1, entries 9–11). Very interestingly, comparable results were obtained when the model reaction was carried out under nitrogen atmosphere instead of aerobic conditions (Table 1, entries 12 *vs.* 2), which is indicative of the efficient confinement effect of the gel network for photoinduced radical reactions in air. On the other hand, green LED irradiation (λ_{max} = 525 nm, 3.8 W) resulted in very low conversion regardless the irradiation time, presumably due to the formation of insufficient concentration of **DPA** triplet states for the TTA process, favoring other deactivation pathways such as phosphorescence or self-quenching (Table 1, entries 13 and 14).

It is also noteworthy that photoreduction of **1** by means of intragel TTA-UC was not specific of gelator **G-1**. In this respect, another model gelator (**G-2**) lacking the carbamate unit and involving a different assembly pattern[32] also provided a suitable supramolecular network for the photolysis of **1** in the presence of **PtOEP** and **DPA** (Table 1, entries 16 and 17). Considering the great structural versatility of LMW gelators and, therefore, the tunable properties of their gels, this result bears special relevance to future optimization of intragel photo processes.

Fig. 4 shows a few more examples of intragel photoreductions in air that strongly support the proof of concept. The observed differences in reactivity can be correlated with the activation barriers, for instance, SET *vs.* back-electron transfer (BET). It is important to emphasize that, as expected, substituted aryl bromides with very high reduction potentials (*e.g.*, alkyl-, MeO-, CF$_3$-, NO$_2$-substituted compounds) showed no photoreduction activity under the conditions. Hence, the reduction potentials of the aryl halides as well as the oxidation potential of **DPA** were obtained in DMF solution by cyclic voltammetry. Taking into account the
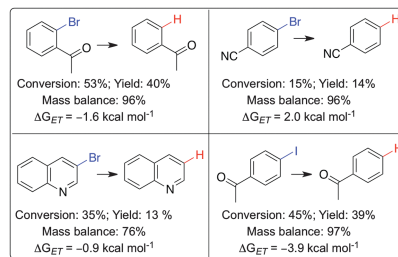

Fig. 4 Additional examples of intragel photoreduction at r.t. in air.

singlet energy of **DPA**, which was found to be 71.5 kcal mol^{-1} in aerated DMF (Fig. S8–S10, ESI‡), and the relative permittivity of the DMF (ε = 36.7), the free energy changes ΔG_{ET} associated with the electron transfer from the **DPA** singlet were obtained using the Weller equation (eqn (1)).[41] Accordingly, SET from ^{1}(**DPA**)* appeared to be thermodynamically feasible for the aryl halides used in this proof of concept study.

$$\Delta G_{ET} \text{ (kcal mol}^{-1}) = 23.06 \times [E_{ox} - E_{red} + (2.6/\varepsilon) - 0.13] - E^*(S_1) \tag{1}$$

A possible reaction mechanism for the intragel photo-reduction of aryl halides by sequential TTA, SET and H-atom transfer (HAT) is outlined in Fig. 5. The process is initiated by the selective excitation of **PtOEP** at 532 nm to generate the ^{3}(**PtOEP**)* state after efficient ISC. Subsequently, **PtOEP** could be restored upon TTET with **DPA**, giving rise to long-lived ^{3}(**DPA**)*. After migration through the stabilizing gel network, a collision between two ^{3}(**DPA**)* molecules effects population of the ^{1}(**DPA**)* state. These species can induce SET to the electrophilic aryl halides, leading to the formation of the unstable radical anions ArX$^{\bullet-}$, which undergo fragmentation affording the corresponding aryl radicals Ar$^\bullet$ and anions X$^-$. Finally, rapid HAT from solvent (DMF) molecules yields the formal reduction product Ar–H (this was confirmed by using DMF-d$_7$, Fig. S6, ESI‡). The formed radical DMF$^\bullet$ may regenerate **DPA** by BET giving highly electrophilic DMF$^+$ species, which are known to be hydrolyzed into volatile products upon work-up.[42] To rule out the possibility of gelator molecules being involved in the trapping Ar$^\bullet$ by N–H abstraction, we performed control experiments using benzene and toluene as solvents. In agreement with the proposed mechanism, no conversion of the starting material was observed in these cases (Table 1, entry 15; Fig. S7, ESI‡).
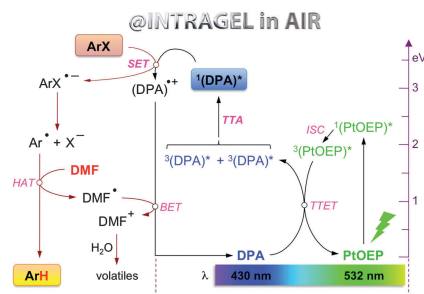

Fig. 5 Plausible mechanism for visible light photoreduction of aryl halides at r.t. in air based on the combination of TTA-UC and SET processes in a gel.

This study demonstrate for the first time the possibility of photoreducing aryl halides through cleavage of the C–halogen bond by means of low-energy visible light irradiation of a proper donor/acceptor system embedded in a physical gel. The strategy is based on the unprecedented combination of a cascade of photophysical and photochemical events involving green-to-blue TTA-UC, SET and HAT as key steps. The gel network provides a suitable stabilizing microenvironment to achieve the challenging multistep process under aerobic conditions, at r.t. and without additional additives such as bases or acids. Good conversions and excellent mass balances were observed with several aryl halides.

In general, large active reaction areas, good diffusion properties, reversibility, reduced overheating effects, multi-stimuli responsiveness, reusability and tunable structural/functional properties are some of the major features of physical gels as confined reaction media or micro/nanoreactors. Considering the great versatility of supramolecular gel networks, high functional group tolerance of low-energy visible light irradiation and other possible combinations of sensitizers and annihilators, there is plenty of room for optimization of such intragel photo-induced processes. Studies toward this direction are currently underway in our laboratories. This proof of concept goes well beyond the classical studies of delayed fluorescence involving TTA and opens the door for future work involving bond activation pathways that are inaccessible in solution under very mild conditions.

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