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Aggregation-Driven Photoinduced α -C(sp³)–H Bond Hydroxylation/ C(sp³)–C(sp³) Coupling of Boron Dipyrromethene Dye in Water Reported by Near-Infrared Emission

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ABSTRACT: Molecular aggregation is a powerful tool for tuning advanced materials' photophysical and electronic properties. Here we present a novel potential for the aqueous-solvated aggregated state of boron dipyrromethene (BODIPY) to facilitate phototransformations otherwise achievable only under harsh chemical conditions. We show that the photoinduced symmetry-breaking charge separation state can itself initiate catalyst-free redox chemistry, leading to selective α -C(sp³)-H bond activation/ C_{sp^3} - C_{sp^3} coupling on the BODIPY backbone. The photoproduction progress was tracked by monitoring the evolution of the strong Stokes-shifted near-infrared emission, resulting from selective self-assembly of the terminal heterodimeric photoproduct into well-ordered J-aggregates, as revealed by X-ray structural analysis. These findings provide a facile and green route to further explore the promising frontier of packing-triggered selective photoconversions via supramolecular engineering.

Multichromophoric aggregates,¹⁻⁴ formed either by selfassembly or by covalently bridged dyes, have led to the emergence of new and useful packing-induced optical properties and functions not present in isolated dyes, such as fluorescence,^{1,5-7} intermolecular charge transfer,⁸⁻¹⁰ singlet fission,¹¹ aggregation-induced emission¹² (AIE), reactive oxygen species (ROS) generation,¹³ etc. In recent years, the photoinduced symmetry-breaking charge separated (SB-CS) state has attracted enormous interest from both biological¹⁴ and materials science perspectives.¹⁵ However, most studies have focused on dimeric and oligomeric constructs of similar dyes,^{11,15,16} which suffer from short-lived SB-CS states.

Extended molecular aggregates, especially those with crystalline order, are promising candidates for the efficient production of long-lived SB-CS states. Such highly ordered packing motifs decisively affect the energy band levels and the extent of excited state delocalization/dynamics.^{1,2,17-19} Besides, they should be conducive to initiating redox chemistry on diffusion-controlled time scales. For instance, distinctive packing patterns of some common dyes²⁰⁻²⁵ have manifested themselves as efficient photocatalysts for hydrogen production,²¹⁻²³ oxygen evolution,²⁰ solar fuels,²⁵ and other organic transformations.²⁴ Boron dipyrromethene (BODIPY) dyes^{26–32} (Figure 1) are known for their excellent photophysical and photosensitizing properties, placing them at the forefront of current research.³³⁻³⁵ Recently, J-aggregates formed by selfassembling some BODIPY dyes are valued for their ability to manifest extraordinary AIE tunability in the visible and NIR regions,^{36–43} with broad prospects for clinical applications.^{44,45} Surprisingly, however, aggregation-driven photochemically

activated transformations at the BODIPY backbone itself remain unexplored.

Here we report a clear departure from the known photochemical stability of the BODIPY framework, upon nanocrystalline aggregation in water, according to the scheme presented in Figure 1. We demonstrate that the SB-CS state itself, rather than the commonly occurring mediating triplet-state, ^{12,13,44} initiates redox chemistry involving ROS, leading to α -C(sp³)–H bond hydroxylation followed by heterodimerization via C_{sp^3} – C_{sp^3} coupling. Almost any source of visible light, including ambient sunlight, can be used to carry out this challenging class of reactions on the BODIPY scaffold, which are otherwise only possible using metal-containing catalysts and strong oxidants. ^{5,6,46–52} Finally, the progress of photoproduction was tracked by monitoring the NIR signal resulting from the selective self-assembly of the terminal photoproduct **2-OH**.

The regular and widely investigated BODIPY 1 forms aggregates in aqueous solutions with high water fraction ($f_w \ge 95\%$) (Supporting Information (SI) page S4; Figure S1). The absorption and fluorescence spectra of 1 in an H₂O/MeCN mixture ($f_w = 98\%$) are significantly affected compared to those in MeCN, displaying well-known features associated with aggregation such as broadening, red-shift, low molar absorptivity

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Figure 1. Schematic illustration of aggregation-triggered photoinduced α -C_{sp}³-H bond hydroxylation and C_{sp}³-C_{sp}³ bond coupling. NIR-AIE of aggregated **2-OH** (red spectrum) versus that of **1**'s aggregates before illumination (yellow).

(ε), reduced fluorescence yield (Φ_f) and multiexponential fluorescence decay (Figures 2a, S2). The average hydrodynamic radius of the aggregates was measured to be 164 ± 4 nm by dynamic light scattering (DLS) (Figure 2a; inset).

The scanning electron microscopy (SEM) photomicrograph shows various sizes of plate-shaped crystalline aggregates ranging from ~0.17 to 0.87 μ m (Figure S3). In addition, their X-ray diffraction (XRD) pattern perfectly matches that of single crystals of 1 (Figure S4), where a J-type arrangement of adjacent units was manifested.⁵

When a solution of aggregates is exposed to visible light, new NIR emission features with high Stokes shift appear (700-850 nm; Figures 2b, S5), the intensity-rise of which becomes steeper and flattens out sooner as the power of the light source increases (Figure 2b; inset). To test whether light-induced transformations caused the emission, aqueous solutions of 1 were irradiated with visible light and the solid residue was analyzed by column chromatography (SI page S3). Two main hydroxylated photoproducts were detected, namely, 1-OH (yield 5.6%) resulting from selective hydroxylation of the α -C(sp³)–H bond of 1 and the α - α -bridged heterodimer, 2-OH (yield 8.2%) formed via 1-OH/1 $\alpha - \alpha C_{sp}^{3} - C_{sp}^{3}$ coupling (Figure 1). The oxidative hydroxylation occurs exclusively and selectively at the α -methyl group position, and no β -hydroxy products were observed. We were also able to detect two minor side reaction products, **bp1** (a β - oxidized derivative of 1) and **bp2** (an α - β ethylene bridged BODIPY dimer) in very low yields (~1% and \sim 1.5% respectively) together with an intractable mixture of polar decomposition products (SI pages S11-25).

Next, we screened the reaction conditions; first, when aggregation is suppressed by decreasing $f_w < 80\%$, illumination has almost no effect on the solute (SI page S4). Second, O₂ removal by degassing dramatically reduces the yield of hydroxylated photoproducts (<1%), whereas O₂ saturation improves their yield by ~50% (7.8% **1-OH** and 12% **2-OH**)





Figure 2. (a) Absorption and fluorescence spectra (exc: 470 nm) of 1 (50.0 μ M) in MeCN and H₂O/MeCN (f_w = 98%) in the dark; *inset*: DLS spectrum of aggregates. (b) Evolution of NIR emission spectra vs illumination time (1 mW white light LED); *inset*: time-dependence of NIR intensity at different LED powers (SI page S3).

compared to normal aerobic conditions. Third, when crystalline aggregates are removed from the aqueous phase by ultracentrifugation, their illumination has no effect. Fourth, shielding the solution from light completely inhibits the reactions. Following illumination of a sample containing the radical trapping reagent 5,5-Dimethyl-1-Pyrroline-N-Oxide (DMPO), the collected electron paramagnetic resonance (EPR) spectrum comprises two radical species (Figure 3b). The main four-line spectrum (*) shows an intensity ratio of 1:2:2:1 and a hyperfine



Figure 3. EPR spectra of aggregates ($[1] = 50 \,\mu$ M) in the presence of 50 mM DMPO (a) before and (b) after illumination and (c) after degassing and illumination. Black lines represent spectral fits (b, c).

coupling constant $a_N = a_{H\beta} = 14.9$ G assigned to the DMPO/ OH• adduct.⁵³ The minor species ($\mathbf{\nabla}$) represents probably a degraded DMPO unknown species with $a_N = 14.7$ G. No signal attributable to the DMPO/OH• adduct was detected under argon atmosphere (Figure 3c and page S26), implying that water oxidation could not be the source of OH•. Yet, the involvement of singlet oxygen $({}^{1}O_{2})$ in the DMPO/OH• adduct formation^{54,55} was excluded by several control experiments listed below: Phosphorescence of ${}^{1}O_{2}$ at ~1270 nm was not observed after pumping a sample of aggregates at 510 nm. The presence of NaN₃, a well-known ¹O₂ quencher, did not suppress the yields of 1-OH and 2-OH. No EPR signal was detected when 2,2,6,6- tetramethylpiperidine (TEMP), a selective spintrapping agent for ${}^{1}O_{2}$, was used (Figure S30). These findings collectively point to a rapid transformation of an initially formed $DMPO/O_2^{\bullet-}$ adduct to the observed stable $DMPO/OH_{\bullet}$.⁵⁶

The potential of aggregates to undergo SB-CS was investigated by femtosecond transient absorption (fs-TA) spectroscopy. In MeCN and below the aggregation threshold ($f_w \le 80\%$), the spectra show the typical decay of the bright excited state to the ground state (Figures 4a, b; S31–33). Upon



Figure 4. (a) fs-TA spectra and (b) 2D-plots for 1 in MeCN and (c), (d) of aggregates of 1 ($f_w = 98\%$; [1] = 30 μ M) respectively; exc: 500 nm.

aggregation, a new weak excited state absorption (ESA) band around 540 nm is observed, which grows with 3 ps lifetime (Figures 4c, d; S34–37). This band has been assigned to a radical anion associated with the formation of a SB-CS state in BODIPY pairs.¹⁶ The cation absorption feature is expected at ~500 nm for 1⁵⁷ and is masked by the ground state bleaching (GSB). The SB-CS state was found to possess multiexponential decay ($\langle \tau \rangle \approx 2.6$ ns) and a long-lived (>50 ns) plateau using ns-TA (Figures S35–37; Tables S1–2). No evidence was found for the triplet manifold population,⁵⁸ whose ESA signature is expected^{59–61} at ~600 nm. Cyclic voltammetry confirms the exergonic CS process in S1, exhibiting an electrochemical gap of 0.71 V, which is well below the optical band gap ($E_{00} = 2.25$ eV) of aggregates (Figures S38–40).

We visualize the reaction sequence as follows (Scheme S1): (a) formation of $O_2^{\bullet-}$ by interfacial electron transfer from the SB-CS state of aggregates of 1 to molecular O_2 , either directly and/or by interference of water radical anions⁶² (H₂O^{$\bullet-$}). (b) the photogenerated radical cationic state at the C–H site of the α -CH₃ group of 1 (whose acidity can be significantly altered in the radical cation state; ^{48,63} pK_a < -10) can be transformed to stable neutral radical by proton transfer to water, considering the exergonic nature of the reaction.^{48,64} (c) $O_2^{\bullet-}$ can react with the cationic state of the α - C–H site of 1 either directly due to its strong nucleophilic character⁶⁵ or (d) because of the strong Brønsted basicity of $O_2^{\bullet-}$, it can be protonated by H₂O even in weakly acidic solutions^{65,66} to form the hydroperoxide radical⁶⁵ HO₂• which can subsequently react with the stable α -centered neutral radical of 1 to form the hydroperoxide derivative. The latter being unstable (the O–O bond strength 34–45 kcal/mol of hydroperoxides is very weak), undergoes thermodynamically favored water-assisted cleavage to afford 1-OH.^{48,67} (e) the latter can promote association with a closely spaced unit of 1 in J-aggregates to form the heterodimer, 2-OH, via $\alpha - \alpha C_{sp}^{3} - C_{sp}^{3}$ oxidative coupling.

The NIR-AIE signal was further evaluated as a "reporter" to monitor the progress of photoproduction. Independent experiments demonstrated that it originates from the selective selfassembly of the terminal photoproduct 2-OH, as explained below. Compared to its monomeric precursors (1 and 1-OH), the highly coplanar structure of 2-OH (Figure 5a) exhibits narrowed and bathochromically shifted absorption and emission spectral features in hexane (Figure 5b), suggesting J-type excitonic coupling between the bridged BODIPY dipoles² (page \$33). In aqueous solutions, the nonfluorescent monomer units of 2-OH aggregate completely when $f_w \ge 80\%$ (Figure 5c). Aggregation is accompanied by the appearance of a strongly Stokes-shifted (~5000 cm⁻¹) NIR emission spectrum (Φ_{f}^{NIR} = 0.12), whose excitation spectrum matches that of the absorption of aggregates (Figure 5c; inset). The concentration-dependent absorption and emission spectra of 2-OH, $(0.05 \le [2-OH] \le 2.0$ μ M) are shown in Figure 5d and 5e, respectively. As seen, the ratio (A_{518}/A_{486}) , the ratio R = (I_{721}/I_{548}) between the NIR intensity at 721 nm and that of the local excited-state (548 nm), as well as the $\Phi_{\rm f}^{\rm NIR}$, soon level off above 0.5 μ M (Figure 5d, 5e insets). Further increasing the 2-OH concentration up to $20 \,\mu M$ has no effect on the absorption spectra (ε vs [2-OH]; Figure 5f); yet the intensity of the NIR emission increases linearly with concentration, highlighting its role as a 'reporter' in monitoring 2-OH photoproduction. Furthermore, the emission lifetime remains unaffected, indicating no changes in the intrinsic properties of the aggregates. (Figure S42). DLS analysis shows a narrow size distribution of particles peaking at 125 nm and remaining invariant above 2.0 μ M. (Figure 5f inset). Consistent with DLS, AFM revealed elongated plates 30-250 nm in size with a peak at 125 nm and a thickness of ~ 10 nm. (Figure 5g). These results indicate a highly favored self-assembly of 2-OH units that evolves over a narrow and low concentration range $(0.05-0.5 \ \mu M)$, resulting in homogeneous single-type assemblies. Single crystals grown from an aqueous solution of 2-OH further confirmed the potential for a packing-mediated, waterstabilized low-energy emitting excited state.^{1,37} The dimeric units are packed (*b*-axis) in a linear arrangement forming ordered, quasi-one-dimensional layers, in which the J-dimers themselves are organized in a slip-stacked (J-type) mode (Figure 5h; SI page S33).

Further investigation revealed that J-aggregates of common, differently substituted BODIPY derivatives also exhibit similar photoconversions associated with their NIR-AIE fingerprints demonstrating BODIPY's J-aggregates' broad potential as photoreactive platforms. (Figure S43). These findings pave the way for engineering the performance of photo(re)active molecular packings by fine-tuning the *structure-packing-energy landscape* relationships. Furthermore, the unique features of in situ generated NIR-AIE such as, tunability, sharpness,



Figure 5. (a) X-ray crystal structure of **2-OH** obtained from hexane. The four alternative OH positions are due to the racemic mixture and crystal packing disorder. R_{AB} is the center-to-center distance between BODIPY rings; θ_{slip} stands for the angle formed by the transition dipole moments (μ_{eg}) and κ is the orientation factor (eq S4); J_c is the calculated energy coupling. (b) Absorption spectra of **1**, **1-OH** and **2-OH** and fluorescence spectrum (dotted line; exc: 470 nm) in hexane. (c) Absorption spectra of **2-OH** in MeCN and H_2O /MeCN mixtures with varied f_w ; *inset*: normalized absorption, fluorescence (exc. 510 nm) and fluorescence–excitation (em. 740 nm) spectra of aggregates of **2-OH**. (d) Normalized concentration-dependent absorption spectra of **2-OH**; *inset*: A_{0-0}/A_{0-1} vs [2-OH]. (e) Concentration-dependent fluorescence spectra as in (d); *inset*: Φ_f^{NIR} and $R = I_{NIR}//I_{LE}$ vs [2-OH]. (f) Absorption and DLS (inset) spectra vs [2-OH]. (g) AFM photograph of crystalline aggregates and distribution of aggregates sizes (lower panel). (h) Long-range order in **2-OH** crystals grown from aqueous solution.

biocompatibility, high luminescence, could benefit applications including high-fidelity bioimaging, frequency-controlled lighting, lasing etc.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.4c02019.

Chemical procedures and methods, NMR and HRMS spectra, CV graphs, additional steady-state and transient spectroscopic data, X-ray diffraction, SEM images and EPR spectra (PDF)

Accession Codes

CCDC 2327954 and 2327956 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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