Supplementary Information for:

# Synthesis, Photophysics and Electronic Structure of Oxobacteriochlorins

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## 1. Survey of oxidants for $H_2$BC-Br$^{3,13}$.

Representative results upon use of several oxidants are listed in Table S1. The reactions were conducted with **$H_2$BC-Br$^{3,13}$** (10 mM) at controlled temperature[43] in anhydrous $CH_2Cl_2$ or freshly distilled $CH_2Cl_2$, with comparable results for the two solvents.

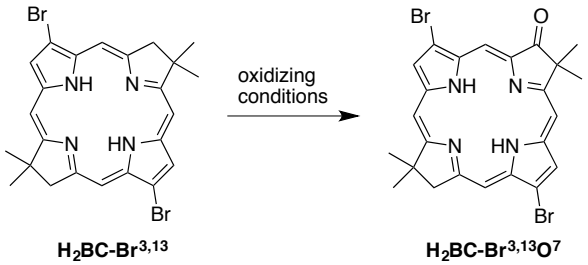
Titration of 5 molar equivalents of $CrO_3$·DMP to **$H_2$BC-Br$^{3,13}$** in $CH_2Cl_2$ at –5 °C gave the mono-oxobacteriochlorin, **$H_2$BC-Br$^{3,13}$O$^7$** in 27% yield (entry 1). Upon titration of the bacteriochlorin with 20 molar equivalents of $CrO_3$·DMP, a more hypsochromically shifted $Q_y$ band at 693 nm was observed, indicating formation of the dioxobacteriochlorin **$H_2$BC-Br$^{3,13}$O$^{7,17}$** (entry 2).

A solution of **$H_2$BC-Br$^{3,13}$** at –30 °C was treated with 2.4 molar equivalents of PCC followed by allowing the temperature to rise to room temperature for 19 h gave a mixture of **$H_2$BC-Br$^{3,13}$** and **$H_2$BC-Br$^{3,13}$O$^7$**. Addition of a further 0.7 molar equivalent of PCC to the reaction mixture at room temperature was done to consume all **$H_2$BC-Br$^{3,13}$**, whereupon **$H_2$BC-O$^7$Br$^{3,13}$** was obtained in 46% yield (entry 3).

The use of 4 equivalents of PDC (entry 4) gave the highest yield (74%). An attempt to trap water and accelerate the reaction by adding molecular sieves gave no improvement (entry 5). However, application of the condition for entry 4 to a 19-mg batch of **$H_2$BC-Br$^{3,13}$** gave a low yield, and over-oxidized product was found (entry 6). The best condition found at this modest scale entailed fewer equivalents of PDC and an extended reaction time (entry 7). The latter

conditions were applied to a 15-mg batch of **$H_2$BC-Br$^{3,13}$**, whereupon following chromatography the desired **$H_2$BC-Br$^{3,13}$O$^7$** was obtained in 59% yield (entry 8).

**Table S1** Survey of oxidation conditions for **$H_2$BC-Br$^{3,13}$**




**$H_2$BC-Br$^{3,13}$** **$H_2$BC-Br$^{3,13}$O$^7$**

| Entry | Oxidant (equiv) | Amt. (mg)[a] | Temp (°C) | Time (h) | Yield (%) |
|---|---|---|---|---|---|
| 1 | $CrO_3$/DMP (5)[b] | 5 | –5 | prompt | 27 |
| 2 | $CrO_3$/DMP (20)[b] | 5 | –5 | prompt | --[c] |
| 3 | PCC (2.4, then 0.7) | 9 | –30 to RT | 19, 3 | 46 |
| 4 | PDC (4.0) | 5 | –30 to RT | 19 | 74 |
| 5 | PDC (3.5), mol sieves 3Å | 6 | –30 to RT | 19 | 73[d] |
| 6 | PDC (3.0) | 19 | –30 to RT | 19 | 15[e] |
| 7 | PDC (0.7, then 0.5) | 15 | –30 to RT | 24, 19[f] | 51[c] |
| 8 | PDC (2.1) | 15 | –30 to RT | 48 | 59 |

[a]The amount of **$H_2$BC-Br$^{3,13}$**. All reactions were carried out with 10 mM bacteriochlorin in $CH_2Cl_2$.

[b]The reagent contained suspended solid and thus the equivalents may not be accurate.

[c]**$H_2$BC-Br$^{3,13}$O$^{7,17}$** was found but not quantitated.

[d]Trace starting material was found.

[e]Trace dioxobacteriochlorin **$H_2$BC-Br$^{3,13}$O$^{7,17}$** was also found and isolated.

[f]Total reaction time was 43 h.

## 2. Chromatographic results upon oxidation of $H_2BC$-$Br^{3,13}MeO^5$.

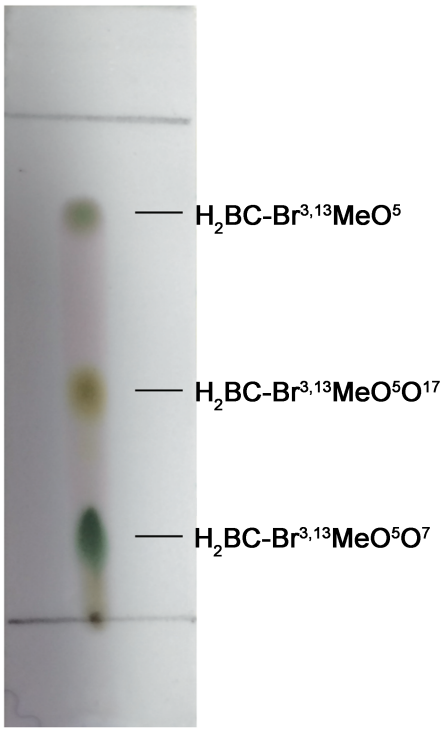



**Figure S1.** Photo of TLC plate following oxidation of **$H_2BC$-$Br^{3,13}MeO^5$**. The TLC plate (silica) was developed with hexanes/$CH_2Cl_2$ (1:1).

## 3. Results of TDDFT Calculations.

**Table S2.** Excited-state compositions and absorption characteristics from TDDFT calculations[a]

| Cmpd | State | Band | H → L | H-1 → L+1 | H-1 → L | H → L+1 | λ (nm) | E (eV) | f |
|---|---|---|---|---|---|---|---|---|---|
| **$H_2BC$** | $S_0 \rightarrow S_1$ | $Q_y$ | 0.92 | 0.06 | | | 711 | 1.74 | 0.367 |
| | $S_0 \rightarrow S_2$ | $Q_x$ | | | 0.76 | 0.24 | 515 | 2.41 | 0.110 |
| | $S_0 \rightarrow S_3$ | $B_x$ | | | 0.22 | 0.77 | 344 | 3.60 | 1.58 |
| | $S_0 \rightarrow S_4$ | $B_y$ | 0.07 | 0.91 | | | 313 | 3.97 | 1.32 |
| **$H_2BC$-$O^7$** | $S_0 \rightarrow S_1$ | $Q_y$ | 0.87 | 0.10 | | | 658 | 1.88 | 0.273 |
| | $S_0 \rightarrow S_2$ | $Q_x$ | | | 0.64 | 0.34 | 525 | 2.36 | 0.024 |
| | $S_0 \rightarrow S_3$ | $B_x$ | | | 0.32 | 0.65 | 372 | 3.33 | 1.59 |
| | $S_0 \rightarrow S_4$ | $B_y$ | 0.10 | 0.87 | | | 340 | 3.64 | 1.11 |
| **$H_2BC$-$O^{7,17}$** | $S_0 \rightarrow S_1$ | $Q_y$ | 0.81 | 0.14 | | | 660 | 1.88 | 0.20 |
| | $S_0 \rightarrow S_2$ | $Q_x$ | | | 0.62 | 0.35 | 550 | 2.25 | 0.014 |
| | $S_0 \rightarrow S_3$ | $B_x$ | | | 0.34 | 0.65 | 374 | 3.31 | 1.72 |
| | $S_0 \rightarrow S_4$ | $B_y$ | 0.14 | 0.84 | | | 358 | 3.46 | 1.19 |

[a] The MOs are abbreviated as HOMO-1 (H-1), HOMO (H), LUMO (L), and LUMO+1 (L+1).