A Molecular Photosensitizer in a Porous Block Copolymer Matrix-Implications for the Design of Photocatalytically Active Membranes

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Figure S1. Size exclusion chromatography of P(S78-co-I22)$_{38}$ and P(S39-co-I11)$_{b}$-P(TEGA$_{14}$-co-VBCl$_{36}$)$_{75}$ in THF, calibration was carried out using polystyrene standards.

Figure S2. $^1$H-NMR of P(S78-co-I22)$_{38}$ and P(S39-co-I11)$_{b}$-P(TEGA$_{14}$-co-VBCl$_{36}$)$_{75}$ (300 MHz, CDCl$_3$).
Table S1: Quantitative XPS analysis of P(S39-co-I11)-b-P(TEGA14-co-VBCl36)75 diblock copolymer membrane before (top) and after (bottom) functionalization with [Ru(bpy)2(ipPhNH2)]2+ photosensitizer. For the analysis the relative sensitivity factors of C 1s (1), O 1s (2.93), N 1s (1.8), Cl 2p (2.29), Ru 3d5/2 (7.39), Ca 2p (5.07), Na 1s (8.52) and Si 2p (0.82) were used.

|        | C  | O  | N  | Cl | Ru | Ca | Na  | Si  |
|--------|----|----|----|----|----|----|-----|-----|
| Polymer membrane | 77.0 | 15.4 | 1.7 | 4.2 | -  | 0.5 | 0.1  | 1.1  |
| Ru-membrane      | 80.4 | 13.5 | 2.1 | 0.5 | 0.1 | 1.2 | -    | 2.2  |

Figure S3. High-resolution C 1s/Ru 3d XP spectra of the P(S39-co-I11)-b-P(TEGA14-co-VBCl36)75 diblock copolymer before (top) and after (bottom) functionalization with [Ru(bpy)2(ipPhNH2)]2+ photosensitizer.

The C 1s XP spectrum of P(S39-co-I11)-b-P(TEGA14-co-VBCl36)75 diblock copolymer (top) shows basically C-C bonds with a shoulder due to C-O bonds from the TEGA units. Furthermore, a small contribution from the COOH group in the TEGA is visible. As expected, no signature of Ruthenium is visible (inset). After functionalization with the [Ru(bpy)2(ipPhNH2)]2+ photosensitizer (bottom), the shoulder of the C 1s peak is modified due to additional C-N bonds. Due to the functionalization, the signatures of the C-O and COOH bonds in the TEGA are attenuated, but still very well visible. Most important, a clear Ru 3d5/2 peak becomes visible close by the C-C peak (inset), confirming the successful functionalization.
**Figure S4.** Digital image of the membrane after functionalization shows intense orange color.

**Figure S5.** Raman spectra of $[\text{Ru(bpy)}_2(ip\text{PhNH}_2)]^{2+}$ with the reference complexes $[\text{Ru(bpy)}_3]^{2+}$ and $[\text{Ru(dmb)}_2(ip)]^{2+}$ in H$_2$O at $\lambda_{ex.}=405$ nm. Orange, green and blue dashed lines correspond to rR bands from $-\text{bpy}$, $-\text{ip}$ and $-\text{PhNH}_2$ respectively. The rR spectra of $[\text{Ru}(4,4'\text{-dmb})_2(ip)]^{2+}$ where $4,4'$-dmb=$4,4'$-dimethyl-2,2'$-bipyridine and ip=$1H$-imidazo[4,5-$f$][1,10]phenanthroline is extracted from elsewhere.$^{[18]}$
Figure S6. Transient absorption anisotropy of $[\text{Ru(bpy)}_2(\text{ipPhNH}_2)]^+$ in TDE with excitation of 400 nm and probe of 600 nm.

Figure S7. Emission spectra of Ru-complex loaded membrane used to calculate emission quantum yield ($\Phi_{em}$) with an integrated sphere.
Preliminary quantum chemical simulations

To further investigate the structural and electronic properties of [Ru(bpy)$_2$ipPhNH$_2$]$^{2+}$, we performed a series of quantum chemical calculations using the Gaussian 16$^{[1]}$ software package. Fully relaxed equilibrium geometries of [Ru(bpy)$_2$ipPhNH$_2$]$^{2+}$ were obtained within the singlet ground state as well as within the triplet ground state (accessible from the singlet ground state equilibrium structure) at the density functional level of theory (DFT) by means of the B3LYP XC functional.$^{[2,3]}$ The def2-SVP basis$^{[4,5]}$ as well as the respective core potentials were applied for all atoms. A vibrational analysis were carried out to verify that minima on the potential energy (hyper-)surface (PES) were obtained.

Subsequently, excited state properties such as excitation energies, transition dipole moments and electronic characters were calculated within the Frack-Condon structure at the time-dependent DFT (TDDFT) level of theory. Therefore, the 100 lowest singlet excited states were calculated (Figure S6). Additionally, the 100 lowest triplet excited states were obtained within the triplet ground state equilibrium structure. Thereby, the same XC functional, basis set and core potentials were applied as for the preceding ground state calculations. Several joint spectroscopic-theoretical studies on structurally related complexes proved that this computational protocol enables an accurate prediction of ground and excited states properties with respect to experimental data, e.g. UV-vis absorption, resonance Raman spectra, (spectro-)electrochemistry and (fs-)transient absorption (i.e. contributions stemming from ground state bleach and excited state absorption) and electron transfer properties.$^{[6–14]}$ A balanced description of excited states featuring, i.e., metal-to-ligand charge transfer (MLCT), ligand-to-metal charge transfer (LMCT), ligand-to-ligand charge transfer (LLCT), intra-ligand charge transfer (ILCT), intra-ligand (IL) and metal-centered (MC) character, as provided by the present computational setup, is essential to assess the photophysics of transition metal complexes. Implicit effects of interaction with a solvent (water: $\varepsilon = 78.3553$, $n = 1.333$) were taken into account on the ground and excited states properties by the solute electron density (SMD) variant of the integral equation formalism of the polarizable continuum model.$^{[15,16]}$ The non-equilibrium procedure of
solvation was used for the calculation of the excitation energies, which is well adapted for processes where only the fast reorganization of the electronic distribution of the solvent is important. Admittedly, these preliminary simulations do not allow to address explicit solvent effects that might alter $[\text{Ru(bpy)}_2\text{iPPhNH}_2]^2^+$'s protonation state in its electron ground state but also in its long-lived charge-separated excited (triplet) state. All calculations were performed including D3 dispersion correction with Becke-Johnson damping.\textsuperscript{[17]}

Furthermore, the (fs-)transient absorption signal of $[\text{Ru(bpy)}_2\text{iPPhNH}_2]^2^+$ was simulated. Therefore, the excited state absorption was modeled based on the simulated spin-allowed triplet-triplet excitation as obtained within the fully relaxed triplet ground state equilibrium structure (DFT), while ground state bleach is given by singlet-singlet reference excitations within the Franck-Condon point, see Figure S7. Additionally, the transient absorption anisotropy was assessed. Therefore, the angles between strongly dipole-allowed singlet-singlet (i.e. excitations into $S_4$, $S_{10}$ and $S_{13}$) and triplet-triplet transitions (i.e. $T_{11}$, $T_{31}$, $T_{34}$ and $T_{47}$), or rather their transition dipole moment vectors, were calculated, see Table S1. All calculations were performed within the input coordinate system (Input Orientation), in order to excluded dependencies with respect to the coordinate system. Due to the marginal structural variations between the fully optimized singlet and triplet ground state equilibrium structures, no reorientation of the triplet ground state structure (with respect to the singlet reference structure) was necessary.
**Figure S8.** Simulated electronic absorption spectrum; prominent excitations are labeled. Excitations into $S_4$ and $S_{10}$ are of mixed 1MLCT/1ILCT character, excitation into $S_{13}$ is of 1ILCT nature. Charge transfer occurs from red to blue.

**Figure S9.** Simulated transient absorption spectrum; prominent excitations are labeled. Spin-allowed triplet-triplet excitations (excited state absorption) within in the triplet ground state equilibrium structure (1ILCT, see $T_1$'s spin density) are labeled in red, ground state bleach contributions are labeled in black (see charge density differences in Figure S4). Charge transfer occurs from red to blue.
Figure S10. Transition dipole moments of prominent singlet-singlet (Figure S4) and triplet-triplet (ESA in Figure S5) transitions.

Table S2. Angles ($\angle$) between transition dipole moments vectors of singlet-singlet excitations ($S_0 \rightarrow S_i$) contributing to the UV-vis absorption of RuipPhNH$_2$ and spin-allowed triplet-triplet excitations ($T_1 \rightarrow T_i$) contributing to its excited state absorption signal. Transition dipole moment vectors are shown in Figure S10.

|       | $S_4$ | $S_{10}$ | $S_{13}$ |
|-------|-------|----------|----------|
| $T_{11}$ | 3.1   | 6.2      | 34.3     |
| $T_{31}$ | 84.6  | 91.5     | 111.1    |
| $T_{34}$ | 7.4   | 5.4      | 30.4     |
| $T_{47}$ | 174.4 | 177.6    | 148.8    |
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