

# Generation and Transfer of Triplet Electron Spin Polarization at Solid-Liquid Interface

Dedicated to Professor Shigeru Yamago on the occasion of his 60th birthday

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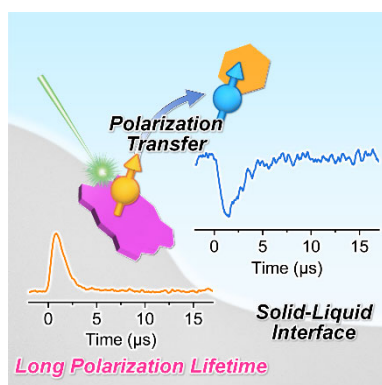
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## ABSTRACT

The photoexcited triplet state of dyes can generate highly polarized electron spins for sensing and dynamic nuclear polarization. However, while triplets exhibit long spin-lattice relaxation times ( $T_1$ ) on the microsecond scale in solids, the polarization quickly relaxes on the nanosecond scale in solution due to the rotational motion of chromophores. Here, we report that the immobilization of dye molecules on a solid surface allows molecular contact with a liquid while maintaining high polarization and long  $T_1$  as in a solid. By adsorbing anionic porphyrins on cationic mesoporous silica gel, porphyrin triplets exhibit high polarization and long  $T_1$  at the solid-liquid interface of silica and toluene. Furthermore, porphyrin triplets on the solid surface can exchange spin polarization with TEMPO radicals in solution. This simple and versatile method using the solid-liquid interface will open the way for utilizing the photo-induced triplet spin polarization in solution, which has been mainly limited to the solid-state.

## TOC GRAPHICS



## KEYWORDS

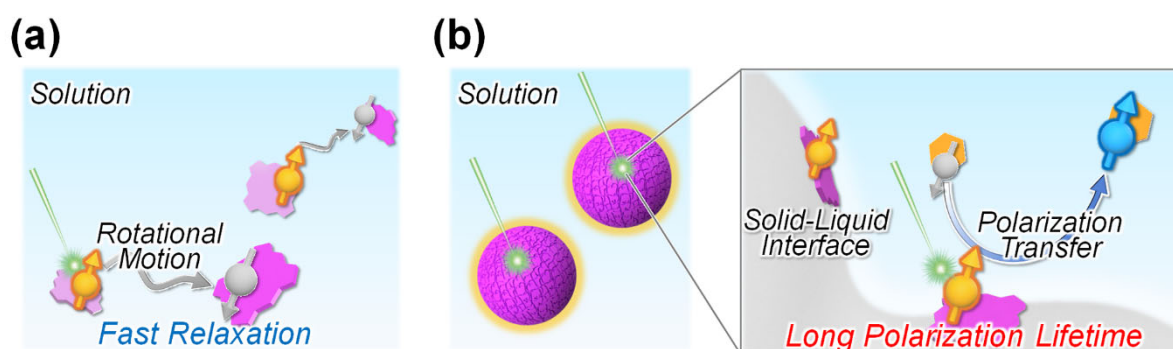
dynamic electron polarization, photoexcited triplet state, solid-liquid interface, porphyrin, radical

## TEXT

The generation of polarized electron spins is the heart of quantum materials.<sup>1-3</sup> In particular, photoexcitation can produce transiently non-equilibrium polarized electron spins even at room temperature.<sup>4-9</sup> Polarized electron spins photo-generated in various materials such as molecular dyes and diamond NV centers have been used to sense external temperature and magnetic fields,<sup>10,11</sup> and to achieve dynamic nuclear polarization (DNP) by transferring polarization from electron spins to nuclear spins.<sup>12-16</sup>

In order to further use polarized electron spins for DNP and ESR imaging of biomolecules in solution, it is desirable to generate polarized electron spins in molecular contact with a liquid. Although many works on Overhauser DNP using electron spins in thermal equilibrium have been reported,<sup>17-21</sup> polarized electron spins are expected to provide even better DNP performance than those using thermally equilibrium electron spins at room temperature. Various mechanisms for electron spin polarization in solution have been reported, including the radical triplet pair mechanism (RTPM),<sup>22-25</sup> the reverse quartet mechanism (RQM),<sup>26,27</sup> and electron spin polarization transfer (ESPT).<sup>28,29</sup> Although highly polarized electron spins can be generated in solids,<sup>3,9,30-33</sup> the rotational motion of molecules in solution causes severe electron spin relaxation (Figure 1a).<sup>34</sup> Recently, DNP of bulk liquid water was achieved by transferring the polarization from electron spins to nuclear spins in a solid and cross relaxation between nuclear spins at the solid-liquid interface, but the small cross relaxation rate remains an issue.<sup>35</sup> Therefore, the key question is how to generate electron spins with high polarization and long polarization lifetime like in solids in a situation where they are in contact with a liquid at the molecular level, and how to make them interact efficiently with molecules in solution.

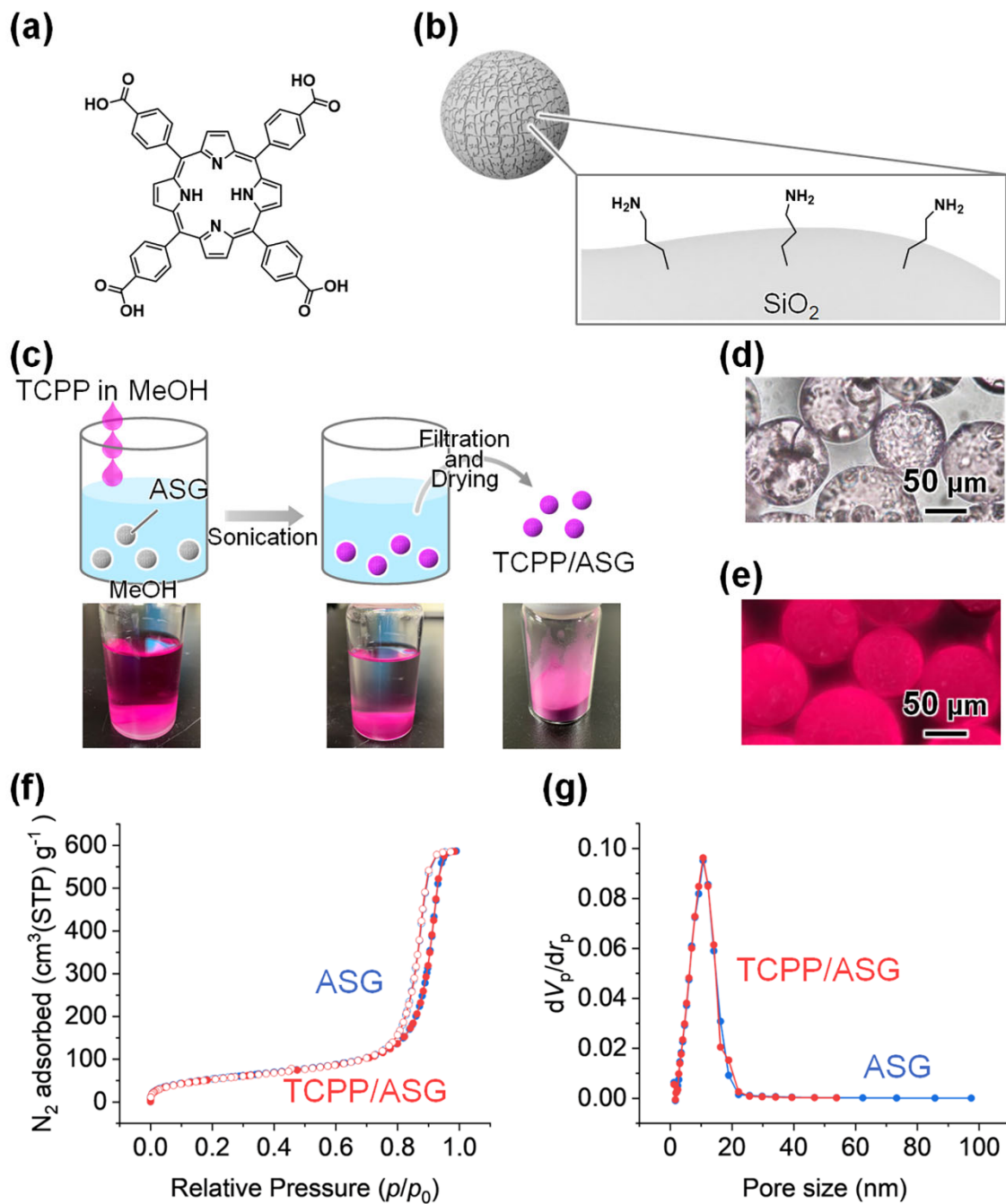
Here we show that dyes placed at the solid-liquid interface can produce highly polarized photoexcited triplets with long spin-lattice relaxation times ( $T_1$ ) and can also exchange electron spin polarization with molecules in solution (Figure 1b). An anionic dye, tetrakis(4-carboxyphenyl)porphyrin (TCPP, Figure 2a), was adsorbed by electrostatic interaction on the surface of mesoporous aminopropyl silica gel (ASG, Figure 2b) with a cationic surface charge. The photoexcited triplet of TCPP was found to be highly polarized at the solid-liquid interface as in the solid state, maintaining a long  $T_1$  of 2.8  $\mu\text{s}$ . Furthermore, the electron spin polarization was transferred from the TCPP triplets to the TEMPO radicals dissolved in toluene, demonstrating that the solid-liquid interface can be used to generate highly polarized triplet electron spins and to exchange its polarization with molecules in a liquid.



**Figure 1.** Schematic representations of (a) immediate relaxation of triplet electron spin polarization in solution and (b) generation of polarized triplet electron spins on the solid surface of mesoporous silica gel and polarization transfer from triplets to radicals in solution.

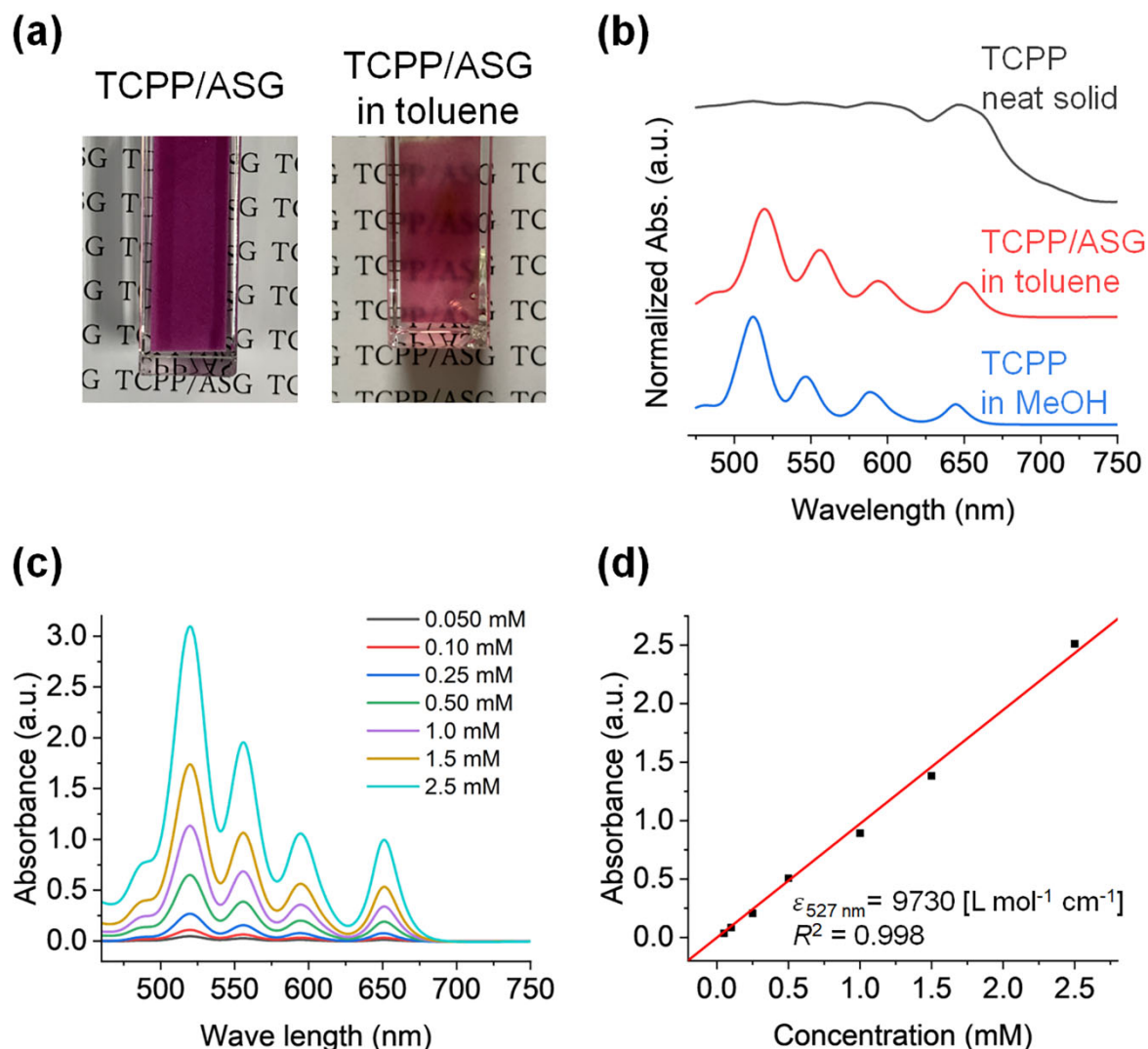
Simply soaking the ASG particles into the TCPP methanol solution caused the solution to become colorless and the ASG to become colored (Figure 2c). From this it could be seen that TCPP was readily adsorbed on the ASG surface. The absorbance of the filtrate obtained by removing TCPP/ASG particles by filtration indicated that 99% of TCPP was adsorbed on ASG (Figure S1). Colored TCPP/ASG particles were obtained by heating and vacuum drying the filtered sample at 60°C (Figure 2c). Under a fluorescence microscope, red emission from

TCPP was observed evenly throughout the ASG particles (Figure 2d, e). Confocal microscopy images of TCPP/ASG particles showed that TCPP-derived fluorescence was observed not only from the outside of the particles but also from the inside (Figure S2). Scanning electron microscopy (SEM) images showed holes of a few tens of nanometers in size on the ASG surface (Figure S3). Nitrogen gas adsorption measurements at 77 K showed that ASG exhibits adsorption isotherms with hysteresis typical of mesoporous materials (Figure 2f). Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) analysis revealed that ASG has a specific surface area of  $175 \text{ m}^2 \text{ g}^{-1}$  and a pore size of around 10 nm, respectively (Figure 2g, Figure S4). The mesoporous structure of ASG was well maintained after being modified with TCPP. The above results indicated that TCPP was adsorbed on the pore surface of mesoporous ASG.



**Figure 2.** Chemical structures of (a) TCPP and (b) ASG. (c) Sample preparation method of TCPP/ASG soaked in toluene. (d) Microscopy and (e) fluorescence microscopy ( $\lambda_{\text{ex}} = 380\text{-}420 \text{ nm}$ ) images of TCPP/ASG. (d)  $\text{N}_2$  adsorption (filled circles) and desorption (open circles) isotherms at 77 K for ASG (blue) and TCPP/ASG (red). (g) Pore distributions of ASG (blue circles) and TCPP/ASG (red circles) by the BJH analysis.

To get insight about the dispersibility of TCPP on the ASG pore surface, absorption and fluorescence spectra of the TCPP/ASG particles were measured in toluene. Due to the relatively close refractive index of toluene and silica, immersion of TCPP/ASG particles in toluene resulted in a sample that is more transparent and suitable for optical measurements (Figure 3a). The concentration of TCPP in the toluene dispersion of TCPP/ASG was set as 1 mM. No absorption of TCPP was observed in the filtrate toluene obtained after the TCPP/ASG particles were removed by filtration, confirming that TCPP was not dissolved in toluene (Figure S5). Absorption spectra of TCPP in methanol indicated that TCPP is molecularly dispersed in methanol at 1 mM (Figure S6), and it showed Q-band-derived peaks at 512, 546, 588, and 645 nm (Figure 3b).<sup>36,37</sup> On the other hand, absorption spectra of TCPP neat solid showed significant broadening due to excitonic interactions between aggregated TCPP.<sup>37,38</sup> Interestingly, TCPP/ASG particles in toluene showed absorption peaks similar to TCPP methanol solution, suggesting the good dispersibility of TCPP on the ASG pore walls. Beer-Lambert plots in toluene also indicated that TCPP was molecularly dispersed on the ASG pore surface in the examined concentration range (Figure 3c, d). The good dispersibility of TCPP on the ASG pore surface was also confirmed by the fluorescence spectra (Figure S7).



**Figure 3.** (a) Images of TCPP/ASG before (left) and after (right) soaked in toluene. (b) Normalized absorption spectra of 1 mM TCPP methanol solution (bottom, blue line), TCPP/ASG in toluene (middle, red line), and TCPP neat solid (top, black line). (c) Concentration-dependent absorption spectra of TCPP/ASG soaked in toluene. The amount of ASG was kept as 0.52 wt% in toluene, and the concentration of TCPP was varied. (d) The absorbance of TCPP/ASG in toluene at 527 nm with different TCPP concentrations.

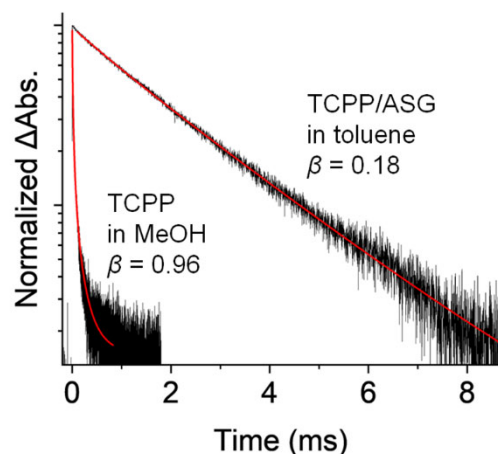
While triplets in solution are quickly deactivated by triplet-triplet annihilation (TTA) associated with dye diffusion and collision,<sup>39</sup> dye adsorption on the solid surface is expected to suppress such deactivation. Transient absorption (Tr-abs) measurements were performed to



characterize the deactivation processes of TCPP triplets in methanol solution and on the ASG surface in toluene. The concentrations of TCPP in the two samples were aligned to the same 1 mM. Samples were excited by pulsed laser at a wavelength of 430 nm and a power of 225  $\mu\text{J}$ , and the time decay of the peak of the transient absorption spectrum around 450 nm was examined (Figure S8). At a glance, the TCPP triplets almost deactivated in microsecond-order in solution, whereas on the ASG surface they decayed over a longer time period of milliseconds (Figure 4). The probability of TTA can be estimated by fitting the experimental results using the following equation,<sup>40</sup>

$$I(t) \propto [T^*]_0 \frac{1-\beta}{\exp\left(\frac{t}{\tau_T}\right)-\beta} \quad (1)$$

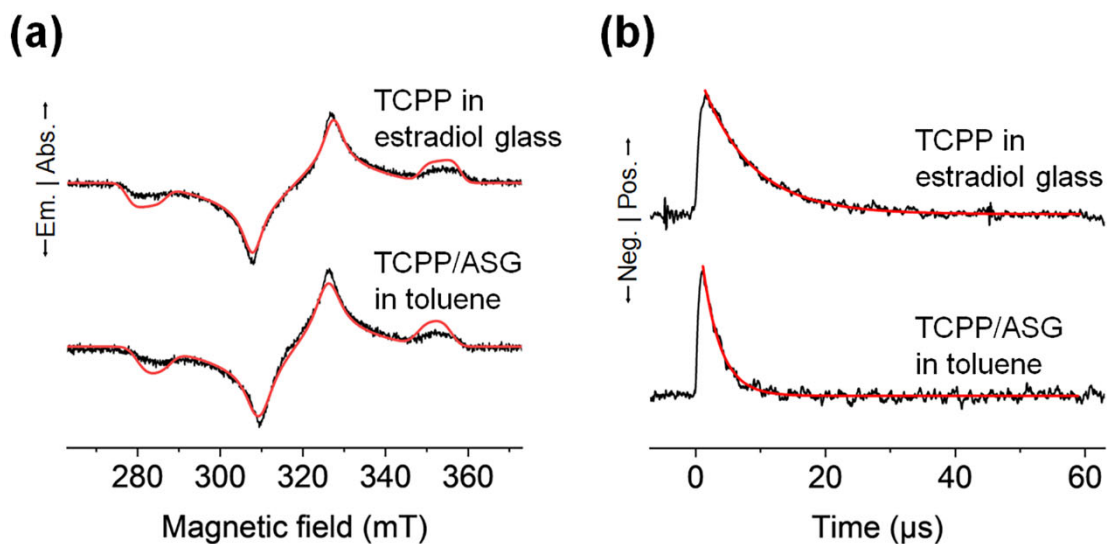
where  $\tau_T$  is triplet lifetime and  $\beta$  is the fraction of triplet decayed by TTA. In methanol, the value of  $\beta$  was estimated to be 0.96, indicating that most triplets were deactivated by TTA. On the other hand, on the ASG surface, the  $\beta$  value was 0.18 indicating that the deactivation of triplets by TTA was much more suppressed. This result indicates that TCPP is strongly adsorbed on the pore surface of ASG and its diffusion is largely suppressed, thus avoiding the deactivation by TTA. The triplet lifetime  $\tau_T$  of TCPP was longer on the ASG surface (2.2 ms) than in methanol (0.26 ms),<sup>41</sup> which is consistent with the interpretation that adsorption on the ASG surface suppresses the mobility of TCPP.



**Figure 4.** Tr-abs decays of 1 mM TCPP methanol solution and 1 mM TCPP/ASG in toluene at room temperature at 450 nm under pulsed excitation at 430 nm. The red lines show fitting results with the equation (1).

Generally, the polarization of photoexcited triplets in solution relaxes very quickly on the nanosecond order due to molecular rotation,<sup>34</sup> but such polarization relaxation is expected to be suppressed if molecular motion is sufficiently suppressed by strong adsorption at the solid-liquid interface. We performed time-resolved electron spin resonance (Tr-ESR) measurements to investigate the electron spin polarization in the photoexcited triplet state of TCPP on the ASG pore surface in toluene at room temperature. The details of the home-built Tr-ESR measurement setup have been reported in our previous work.<sup>42</sup> The ESR spectra were measured in the direct detection mode of an oscilloscope using X-band (9 GHz) microwaves with an amplitude of -10 dBm and 527 nm pulsed laser. The photoexcited triplet of TCPP adsorbed on the ASG surface exhibited ESR spectra typical of porphyrin triplets in solids and did not show motional narrowing as in solution (Figure 5a).<sup>34,37,38,43</sup> In fact, when compared to the triplet ESR spectra of TCPP doped in estradiol glass, the zero-field splitting parameters and relative polarization ratio were almost similar (Table 1).<sup>44</sup> Remarkably, the spin-lattice relaxation time ( $T_1$ ) of the TCPP triplet was 2.8  $\mu$ s on the ASG surface, significantly longer than in solution (Figure 5b).<sup>34</sup> This value was shorter than that of the TCPP triplet in estradiol

glass (7.7  $\mu\text{s}$ ), indicating that the triplet is slightly mobile at the solid-liquid interface. It is a reasonable result that a little mobility remains at the solid-liquid interface. It is noteworthy that the long  $T_1$  on the order of microseconds was obtained in contact with the liquid at the molecular level.



**Figure 5.** (a) Tr-ESR spectra of 1 mM TCPP in estradiol glass (top) and 1 mM TCPP/ASG in toluene (bottom) at room temperature. The simulation results by using EasySpin in MATLAB are shown (red lines).<sup>44</sup> (b) Decays of ESR signal of 1 mM TCPP in estradiol glass at 327 mT (top) and TCPP/ASG in toluene at 327 mT (bottom) at room temperature. Single-exponential fitting results are also shown (red lines).

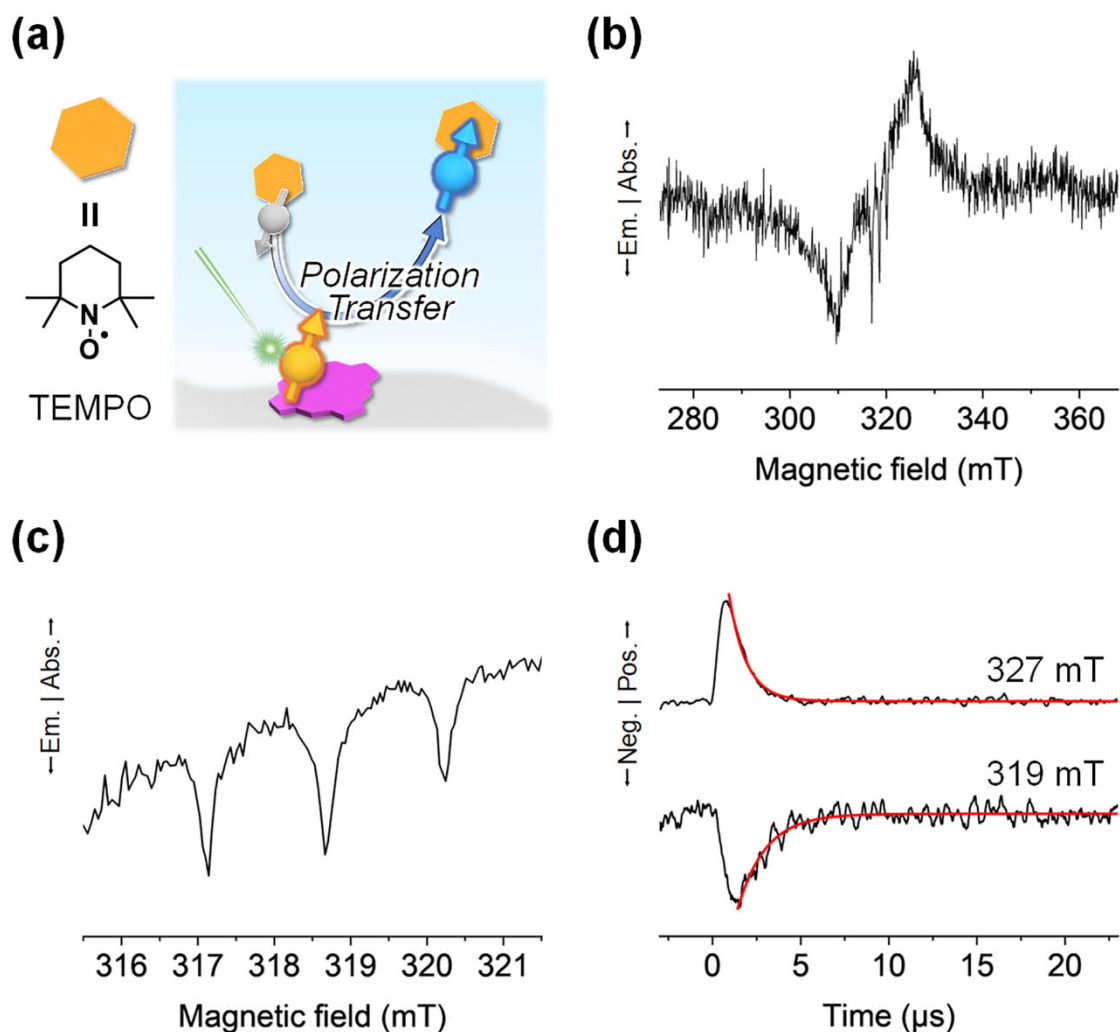
**Table 1.** Zero-field splitting parameters and relative zero-field populations derived from the simulation of the Tr-ESR spectra of 1 mM TCPP in estradiol glass and 1 mM TCPP/ASG in toluene are shown in Figure 5a.

|                         | $ D $ (MHz) | $ E $ (MHz) | $P_x$ | $P_y$ | $P_z$ |
|-------------------------|-------------|-------------|-------|-------|-------|
| TCPP in estradiol glass | 1130        | 195         | 0.21  | 0.75  | 0.04  |
| TCPP/ASG in toluene     | 1062        | 198         | 0.20  | 0.76  | 0.04  |

To demonstrate whether the spin polarization can be exchanged between TCPP adsorbed on the ASG surface and molecules in solution, transient ESR measurements were performed by dissolving TEMPO, a typical stable radical, in toluene (Figure 6a). The absence of any change in the state of TCPP by the addition of TEMPO was confirmed from the absorption, emission, and transient absorption spectra (Figure S9). When samples of 1 mM TCPP/ASG immersed in 10 mM TEMPO toluene solution were excited with the 527 nm pulsed laser for Tr-ESR measurements, three sharp emissive peaks around 319 mT were observed in addition to a broad signal from the TCPP triplet (Figure 6b, c). The shape of these signals was consistent with the TEMPO-derived signals observed in continuous-wave (cw) ESR measurements of the same sample in the absence of light irradiation (Figure S10), indicating that the photoexcitation produced electron spin polarization of TEMPO radicals in solution. The observed isotropic ESR spectrum can be assigned to TEMPO dissolved in solution.<sup>45</sup>

An indication of the mechanism of radical polarization generation was obtained from the time variation of the ESR signal intensity (Figure 6d). The triplet-derived signal at 327 mT decayed at 0.99  $\mu$ s, and the radical-derived signal at 319 mT also decayed with a similar time constant of 1.6  $\mu$ s. This suggests that the polarization transfer from the TCPP triplet to the TEMPO radical occurred by the electron spin polarization transfer (ESPT)<sup>28,29</sup> mechanism. In ESPT, the spin exchange between the triplet and the radical generates a polarization of the radical instead of losing the net polarization of the triplet. The spin-lattice relaxation time of the TEMPO radical is as short as ca. 1  $\mu$ s,<sup>46</sup> so that the polarization transfer process is rate-limiting and the signal decay of the TEMPO radical becomes close to the TCPP triplet spin-lattice relaxation time. Since the net polarization of the free-base porphyrin is known to be negative,<sup>28</sup> the observation of negative polarization of TEMPO also supports the ESPT mechanism. Other possible mechanisms include the radical triplet pair mechanism (RTPM)<sup>22-25</sup> and the reversed quartet mechanism (RQM).<sup>26,27</sup> In RTPM, collisions and dissociations

between triplets and radicals generate radical polarization. Since the triplets need not be polarized in RTPM, the radical polarization signal is observed not during the triplet spin-lattice relaxation time, but rather during the lifetime of the triplet excited state in the thermal equilibrium. In the present study, the decay time constant of the radical polarization signal was 1.6  $\mu\text{s}$ , which is much shorter than the triplet lifetime of TCPP in the presence of TEMPO (627  $\mu\text{s}$ , Figure S11), and thus is not due to RTPM. The RQM mechanism requires maintaining a strong exchange interaction between the triplet and the radical, but RQM would not occur because the TEMPO radical is free to move in solution. Therefore, it is indicated that ESPT from TCPP on the ASG surface to TEMPO radicals in toluene takes place, and that the photoexcited triplet can indeed exchange polarization with molecules in solution at the solid-liquid interface.



**Figure 6.** (a) Schematic illustration of polarization transfer from TCPP to TEMPO on the ASG surface. (b) Tr-ESR spectra of 1 mM TCPP/ASG soaked in 10 mM TEMPO toluene solution. (c) Tr-ESR spectra of 1 mM TCPP/ASG soaked in 10 mM TEMPO measured for a specific magnetic field range (315.5-321.5 mT). (d) Decays of ESR signal (black lines) of 1 mM TCPP/ASG soaked in 10 mM TEMPO toluene solution at 327 mT (top) and 319 mT (bottom). Single-exponential fitting results are also shown (red lines).

In conclusion, we demonstrate that the solid-liquid interface can be used to form a highly polarized photoexcited triplet in contact with a liquid at the molecular level, and that it can exchange the polarization with radical electron spins in the liquid. In solution, the triplet is readily deactivated by TTA associated with molecular diffusion, but the chromophore

diffusion can be largely suppressed by the electrostatic adsorption on the ASG solid surface and TTA between the TCPP triplets is significantly reduced to occur. Moreover, while the polarization of the triplets relaxes quickly due to the rotational motion of the chromophores in solution, the triplets of TCPP immobilized on the ASG surface exhibit the long spin-lattice relaxation time of 2.8  $\mu$ s. By using mesoporous ASG with a relatively large surface area and pore size, TCPP triplets with concentrations as high as 1 mM can exchange polarization with molecules in a liquid while being polarized as in a solid. This very unique situation would lead to ESR imaging and DNP bioanalysis by polarizing the electron and nuclear spins of molecules in solution. The present method, physically adsorbing dyes on the surface of mesoporous materials, is extremely simple and versatile, and will provide a new quantum sensing platform when applied to various photo-induced spin polarization materials that have been actively studied in the solid state in recent years.

## **ASSOCIATED CONTENT**

### **Supporting Information.**

The following files are available free of charge.

Experimental details, absorption and fluorescence spectra, confocal microscopy images, SEM images, BET plots, cw-ESR spectra, and transient absorption spectra and decays.

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## **Notes**

The authors declare no competing financial interest.

## **ACKNOWLEDGMENT**

We appreciate Prof. Masa-aki Morikawa and Prof. Nobuo Kimizuka at Kyushu University for the access to the confocal microscope. This work was partly supported by the JST-FOREST Program (JPMJFR201Y), JSPS KAKENHI (JP20H02713, JP22K19051, JP21J13049, and JP22J21293), The Murata Science Foundation, Research Foundation for Opto-Science and Technology, and Kyushu University Platform of Inter-/Transdisciplinary Energy Research (Q-PIT) through its “Module-Research Program”.



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