

Organic Ion-Pair Charge-Transfer (IPCT) Nanoparticles: Synthesis and Photoinduced Electrochromism

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IR spectra of the BzV-TPB precipitate together with those of pure BzV (dichloride salt) and TPB (sodium salt).

IR spectra of pure BzV and TPB along with the BzV-TPB precipitate are shown in Figure S1. The precipitate was completely washed with water. The IR spectrum of the precipitate has characteristic features both of BzV and TPB.

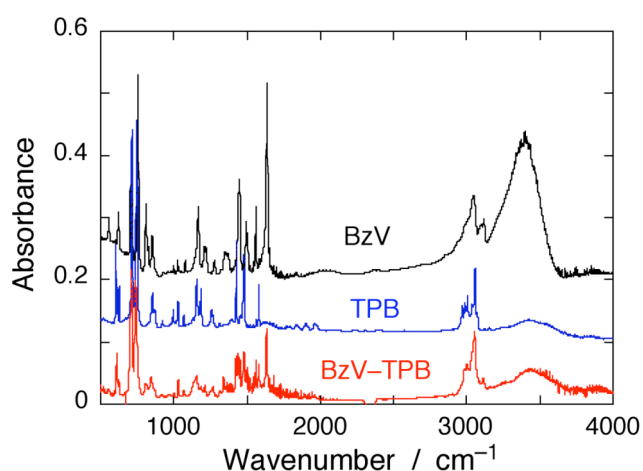


Figure S1. IR spectra of BzV-TPB (precipitate), BzV (dichloride) and TPB (sodium salt).

Characterization of the precipitates produced after photoirradiation of VP^{IPCT} nanoparticles synthesized at $\rho = 1$.

(I) The precipitates produced after photoirradiation of the VP^{IPCT} nanoparticles synthesized at $\rho = 1$ was characterized by IR spectroscopy. The spectra were measured with a Horiba FT-720 infrared spectrophotometer by the KBr disk pellet method. The result is shown in Figure S2a.

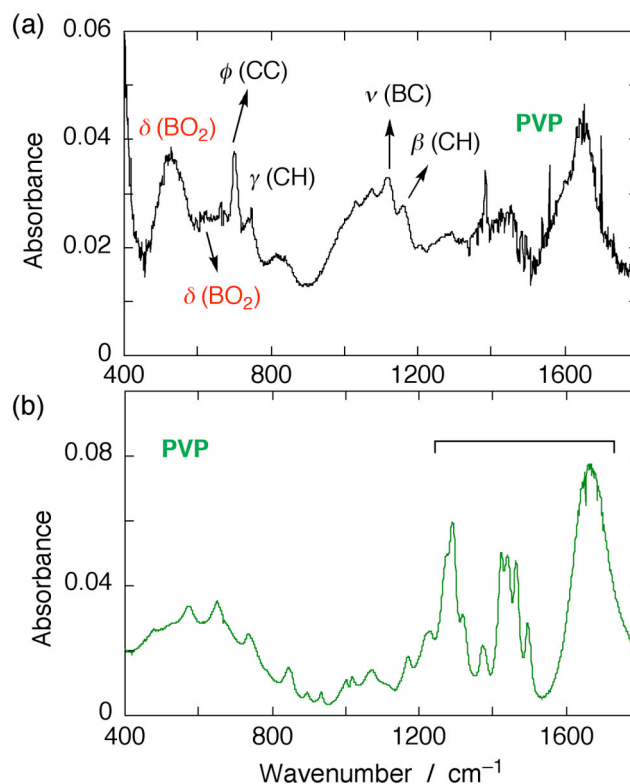


Figure S2. IR spectra of the precipitate and PVP.

Figure S2b also shows IR spectrum of pure PVP in the wavenumber region of 400–1800 cm⁻¹. Note that this energy region has significant information on the vibrational modes of borate derivatives. Indeed, according to the literature,¹ characteristic bands of B–O deformation $\delta(\text{BO}_2)$ at ~530 (in-plane mode) and ~630 cm⁻¹ (out-of-plane mode) can be recognized in the spectrum, suggesting the formation of boronic acid derivatives. The B–C stretch mode $\nu(\text{BC})$ is also observed at ~1110 cm⁻¹. The intense peak observed at ~750 cm⁻¹ is assigned to the deformation mode of C–H $\gamma(\text{CH})$, and ~690 cm⁻¹ is due to out-of-plane ring deformation of phenyl substituents $\phi(\text{CC})$.

(II) The negative-ion ESI mass analysis of the precipitate formed after photoirradiation of the VP^{IPCT} nanoparticles synthesized at $\rho = 1$ was conducted using a mass spectrometer (JMS-T100LC, JEOL). The result is shown in Figure S3.

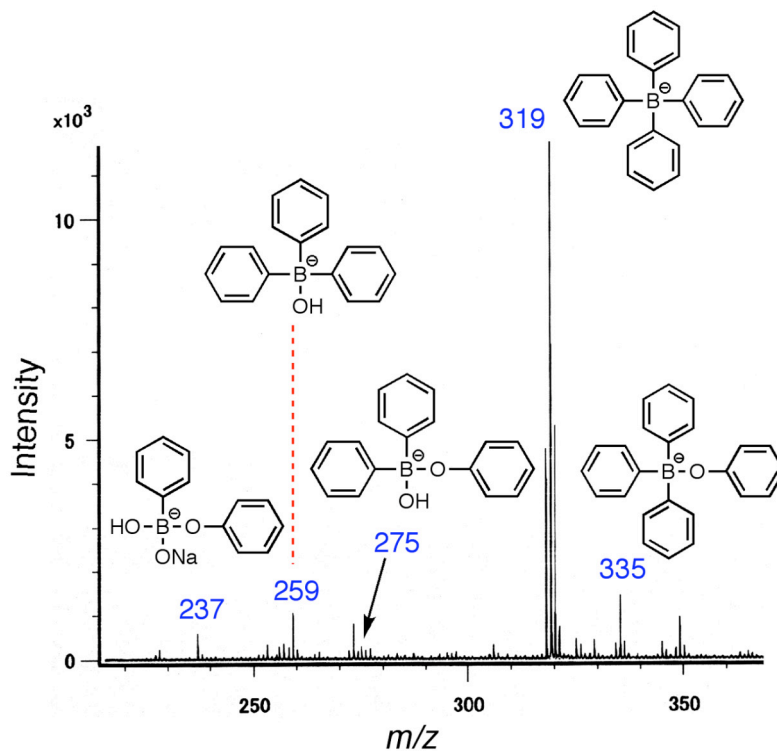


Figure S3. Negative-ion ESI mass spectrum of the precipitate.

An intact molecular ion peak of TPB^{\ominus} was strongly observed at $m/z = 319$. In addition, several peaks originated from decomposed compounds of oxidized TPB^{\ominus} were also detected at $m/z = 237$, 259 , 275 , and 335 . The possible peak assignments are also indicated in the figure.

On the basis of the above-mentioned discussion (I) and (II), decomposition of TPB (or oxidized TPB) is obvious, so the behavior should contribute to the long-lived ET state observed.

Durability of the VP^{IPCT} nanoparticle systems.

To examine how durable these coloring/decoloring processes are, we repeated the photochromic activation-deactivation cycle several times. The results are shown in Figure S4.

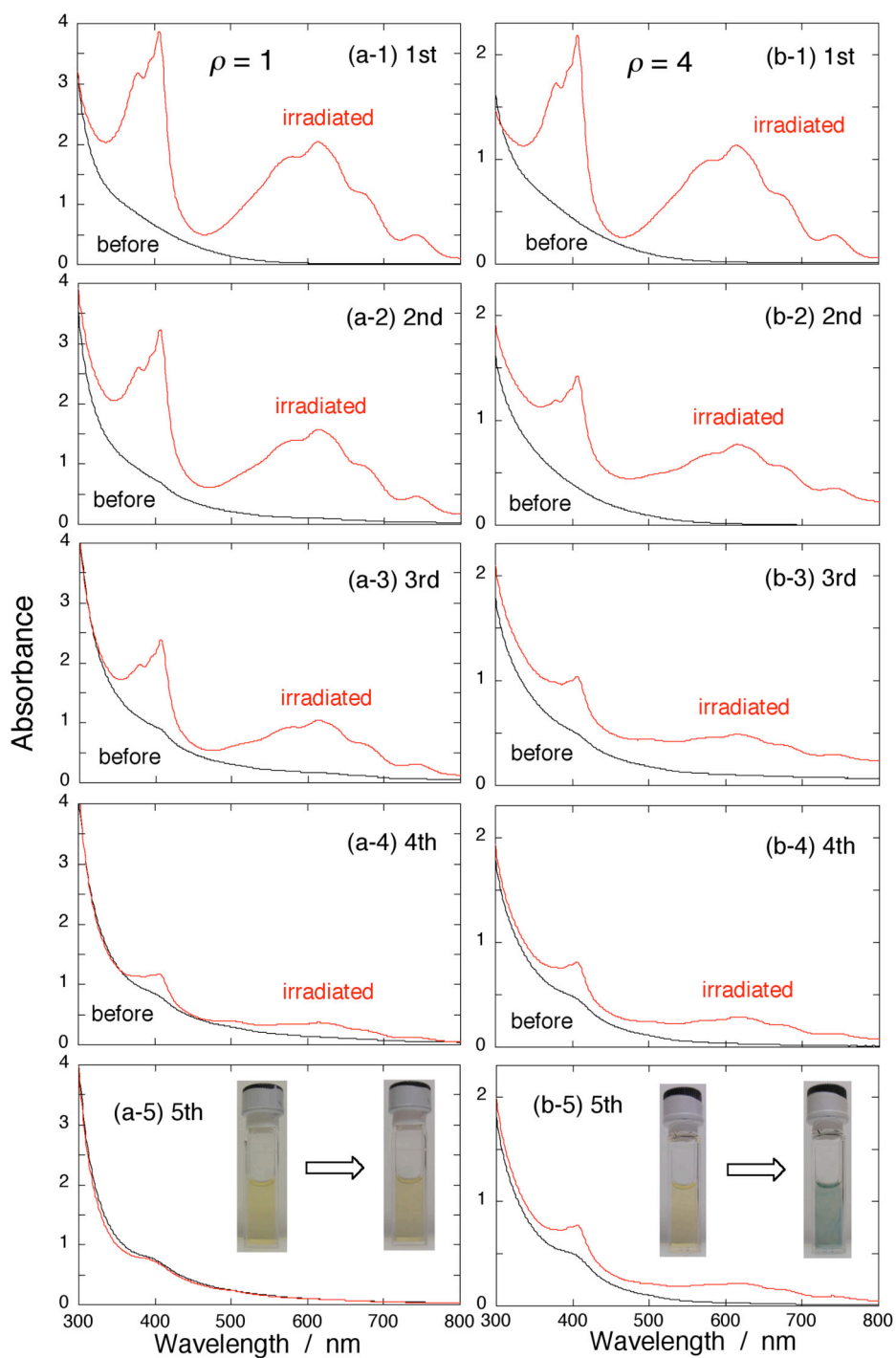


Figure S4. Repeated cycles of photoactivation-deactivation process conducted for the nanoparticle samples.

The first activation was carried out for the freshly prepared VP^{IPCT} nanoparticle samples by irradiating the UV light at 365 nm for 10 min. The absorption spectra for the samples with $\rho = 1$ and 4 are shown in Figures S4a-1 and S4b-1, respectively. Note here that sample with $\rho = 1$ became turbid, whereas that with $\rho = 4$ was still transparent. After one-day storage of the samples under dark, they were again irradiated with the UV light (2nd activation as shown in Figures S4a-2 and S4b-2 for samples with $\rho = 1$ and 4, respectively), followed by further storage for one day. Then, similar photoactivation-deactivation cycle was repeated five times. According to the spectra, the formation yield of photo-generated $\text{BzV}^{+\bullet}$ in each cycle gradually decreased with an increase in the cycle number in both nanoparticle samples, meaning that the repeated coloring-decoloring process resulted in the suppression of $\text{BzV}^{+\bullet}$ radicals. However, even after several cycles of photoactivation and deactivation, interestingly, the yellow CT bands could still be observed. This indicates that, on one hand, decomposition of oxidized TPB (= TPB^\bullet) takes place in the sample (particularly prepared at $\rho = 1$), but at the same time, structural (or orientational) rearrangements of BzV^{2+} and TPB^- (acceptor-donor CT pairs) can occur in the nanoparticles to produce different IPCT species, which brings about a very fast reverse ET reaction and thus almost no color change.

Characterization of degradation products of BzV in the VP^{IPCT} nanoparticle sample ($\rho = 1$) after photoirradiation.

The positive-ion ESI mass analysis for the supernatant solution of nanoparticle sample ($\rho = 1$) formed after photoirradiation was conducted using a mass spectrometer (JMS-T100LC, JEOL). The result is shown in Figure S5.

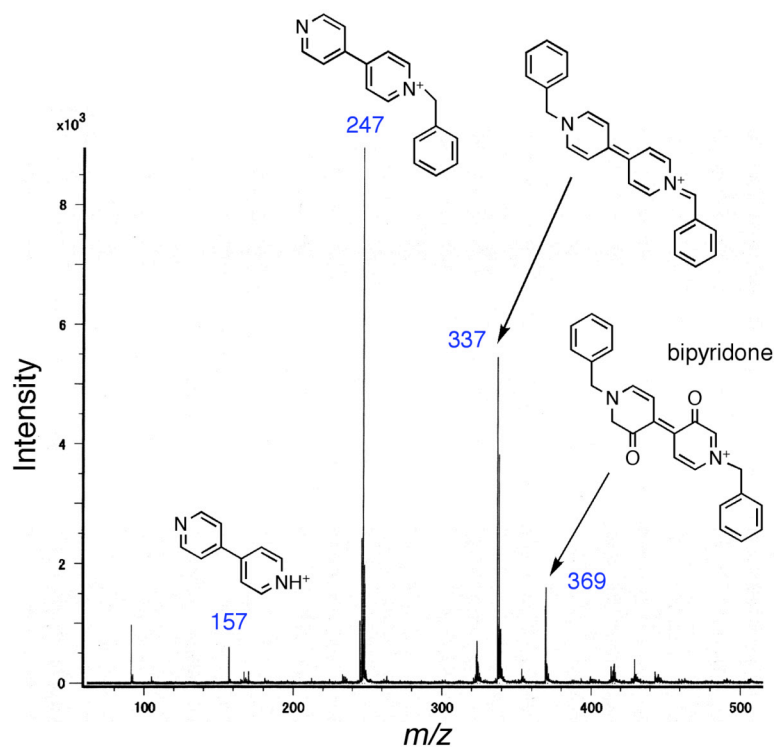


Figure S5. Positive-ion ESI mass spectrum of the supernatant of VP^{IPCT} nanoparticle sample ($\rho = 1$) produced after photoirradiation.

A strong peak at $m/z = 247$ is due to the main fragment of BzV, and that at $m/z = 337$ can be ascribed to a slightly modified compound of BzV. Importantly, the peak at $m/z = 369$ is originated from the oxidized compounds of BzV, one of the bipyridone compounds. The possible peak assignments are also indicated in the figure. Note that the carbonyl groups in bipyridone compounds can be located either at 2- or 3-position.

Characterization of the VP^{IPCT} nanoparticle samples ($\rho = 1$ and 4) including both the precipitate and supernatant after photoirradiation.

The negative-ion ESI mass spectra of the whole nanoparticle samples with $\rho = 1$ and 4 obtained after 1 day after UV irradiation are shown in Figure S6.

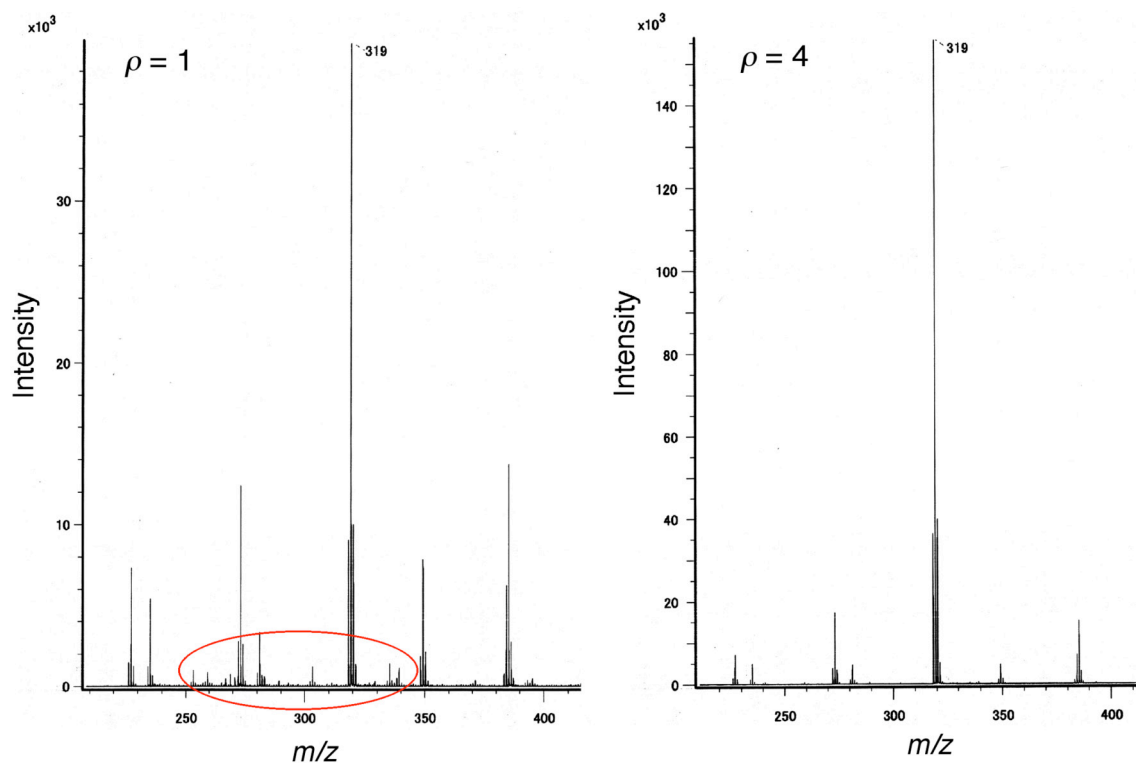


Figure S6. Negative-ion ESI mass spectra of the nanoparticle samples with $\rho = 1$ and 4 kept for 1 day after UV irradiation.

In comparison between these spectra, the sample with $\rho = 1$ solely had several peaks assigned to the degradation products of TPB (or oxidized TPB) in the m/z region of 250–300, proving the absence of TPB decomposition upon photoirradiation.

References

- (1) Faniran, J. A.; Shurvell, H. F. Infrared spectra of phenylboronic acid (normal and deuterated) and diphenylphenylboronate. *Can. J. Chem.* **1968**, *46*, 2089–2095.