# Electronic Supplementary Information (ESI)

## Tunable photochemical properties of covalently anchored and spacially confined organic polymer in layered compound

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## FESEM images of the starting materials

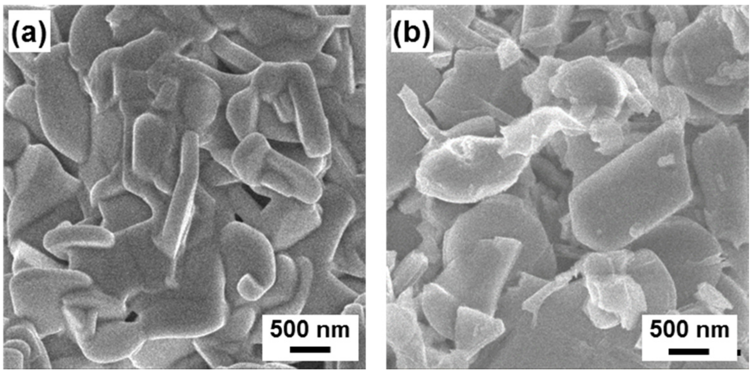

**Fig. S1**. FESEM images of the Cs–$TiO_2$ (a) and H–$TiO_2$ (b).

The platy morphologies of the VBA–$TiO_2$ were not remarkably changed from those of the precursor Cs–$TiO_2$ and H–$TiO_2$.

### FT-IR spectra and TG curves of the VBA-$TiO_2$

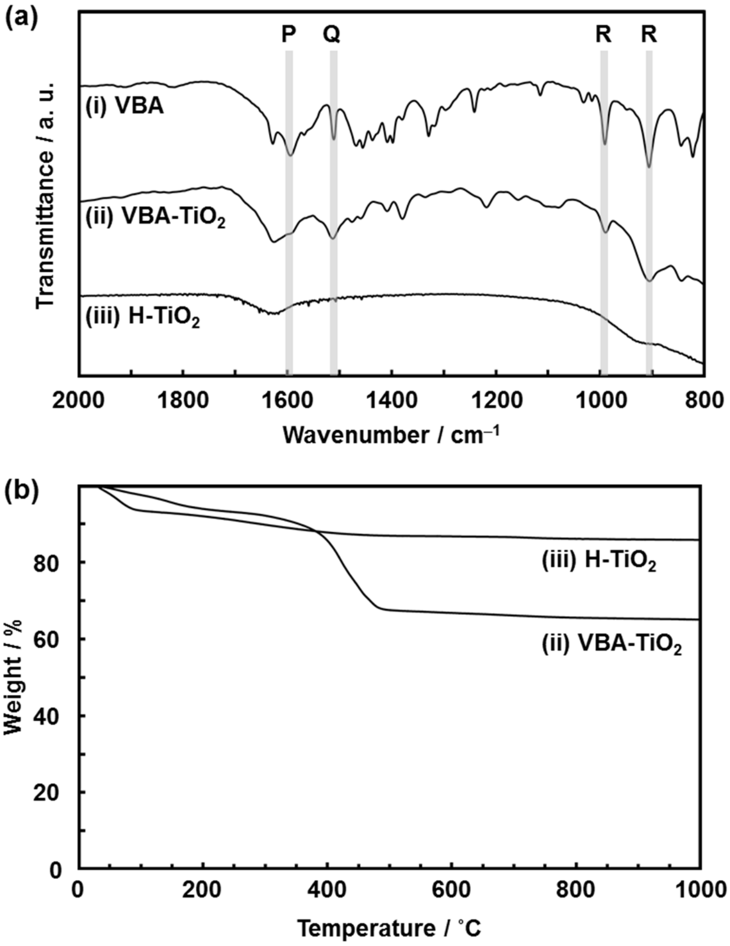

**Fig. S2**. FT-IR spectra (a) and TG curves (b) of VBA molecule (i), the VBA–$TiO_2$ (ii), and H–$TiO_2$ (iii). In the FT-IR spectra, the absorption bands of P, Q, and R are assigned to the following vibrations: N–H asymmetric (P) and symmetric (Q) bending vibration of primary amine salt and C–H out-of-plane bending vibration of vinyl group (R).

The FT-IR spectra indicate the formation of VBA–$TiO_2$ composite (Fig. S2a). In the TG curve, the weight loss around 300 ˚C and 400 ˚C corresponds to the incorporated water molecule and the interlayer VBA, respectively (Fig. S2b). Based on the TG curve, the chemical formula of the VBA–$TiO_2$ composite was estimated to be $H_{0.370}(VBA)_{0.330}Ti_{1.825}\square_{0.175}O_4 \cdot xH_2O$ ($x<0.94$, □: vacancy).

### FT-IR spectra and TG curves of the PVCz/VBA–$TiO_2$

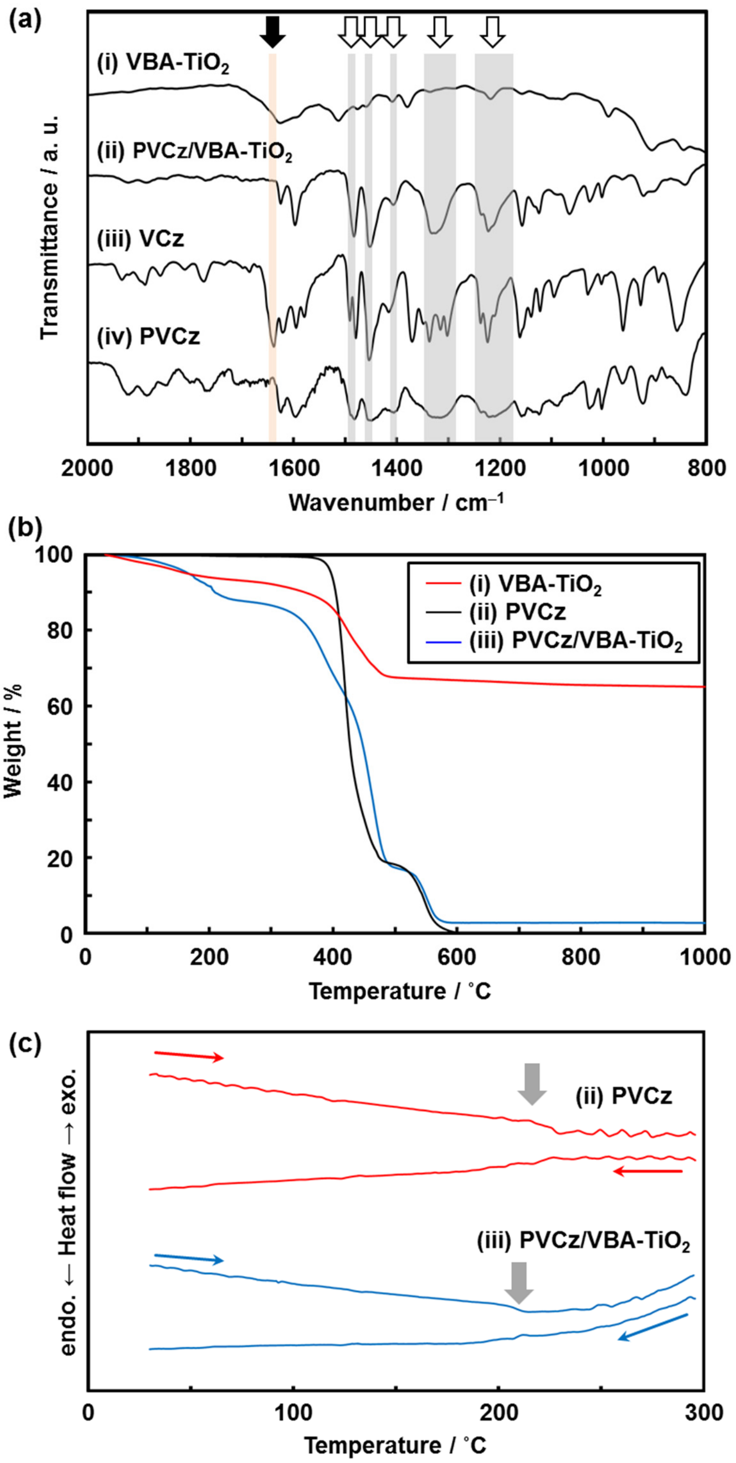

**Fig. S3**. FT-IR spectra (a), TG curves (b), and DSC thermograms (c) of the VBA–$TiO_2$ (i), the PVCz/VBA–$TiO_2$ (ii), VCz (iii), and PVCz (iv). In the FT-IR spectra, the white and black arrows indicate the characteristic absorption of the PVCz and vinyl groups, respectively.

The FT-IR spectrum of the PVCz/VBA–$TiO_2$ showed the appearance and disappearance of the characteristic absorption corresponding to the PVCz (white arrow) and vinyl group (black arrow), respectively (Fig. S3a). In the TG curve, both VBA and PVCz showed the weight loss around 300–600 ˚C. The content of PVCz, namely 83%, was estimated from the difference of the weight loss between VBA–$TiO_2$ and PVCz/VBA–$TiO_2$. The DSC thermograms of the PVCz/VBA-$TiO_2$ showed the baseline shift around 200 ˚C similar to that observed on the commercial PVCz. The baseline shift is ascribed to the glass transition of the PVCz. The results supported the formation of the polymer chains in the layered structure.

## UV-Vis spectra of the PVCz/VBA–TiO₂ and its reference samples

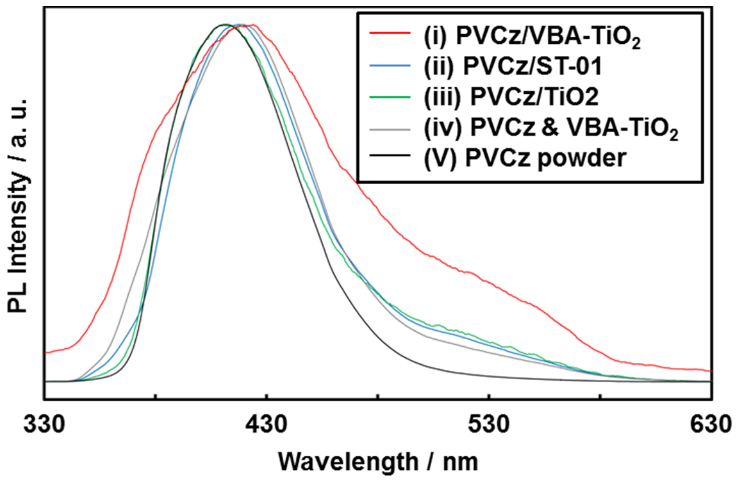

**Fig. S4**. UV-Vis spectra of the PVCz/VBA–$TiO_2$ (i) and its reference samples (ii)–(v). Commercial PVCz was mixed with $TiO_2$ nanoparticles (ST-01, ii), microparticles (iii), and the VBA–$TiO_2$ (iv). PVCz powder was synthesized by the same procedure in the absence of VBA–$TiO_2$ (iv).

The PVCz/VBA–$TiO_2$ copolymerized composite only showed the characteristic emission band longer than 470 nm. The extension of the peak is ascribed to the formation of J-aggregate. The characteristic emission spectrum was not observed on the reference samples, as shown in the spectra (ii)–(v) in Fig. S4.

### UV-Vis spectra of TPE and BPEA in the solid state

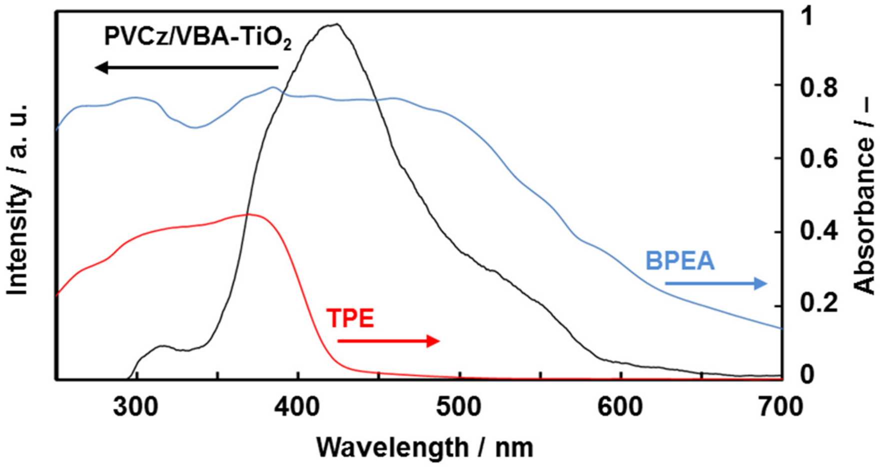

**Fig. S5.** Fluorescence spectrum of the PVCz/VBA–$TiO_2$ and UV-Vis spectra of the TPE and BPEA powders.

Since the fluorescent peak of donor PVCz and the absorption peak of acceptor TPE and BPEA are overlapped, formation of the D-A complexes, such as TPE/PVCz/VBA–$TiO_2$ and BPEA/PVCz/VBA–$TiO_2$, induces the emission based on fluorescence resonance energy transfer (FRET).

## Fluorescence spectra of TPE and BPEA in the solid and solution states

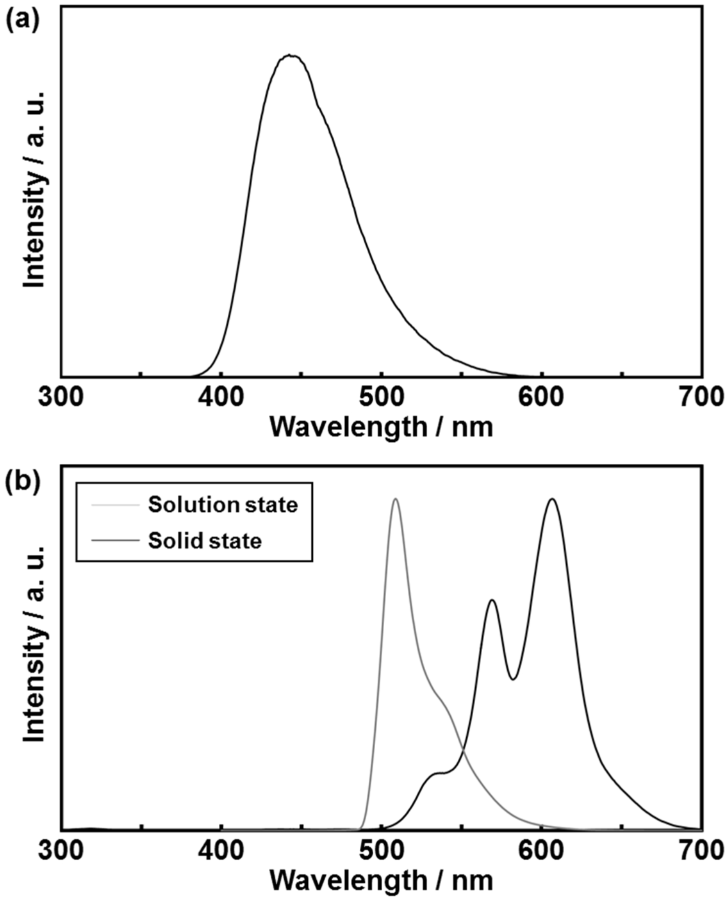

**Fig. S6**. Fluorescence spectra of TPE in the solid state (a) and BPEA in the solid (black line) and solution (gray) states (b).

The TPE/PVCz/VBA–$TiO_2$ and BPEA/PVCz/VBA–$TiO_2$ showed the emission based on FRET (Fig. 7b). The peak positions are similar to those of the TPE and BPEA in Fig. S6.