Supplementary information

Electrical monitoring of photoisomerization of block copolymers intercalated into graphene sheets

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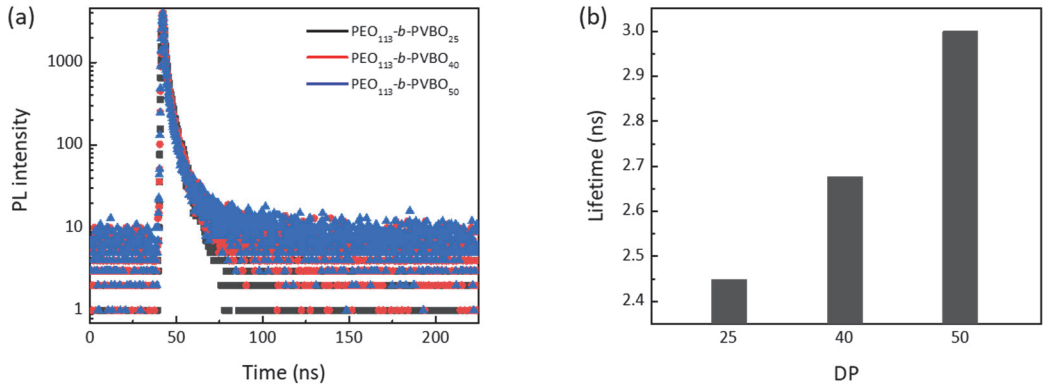
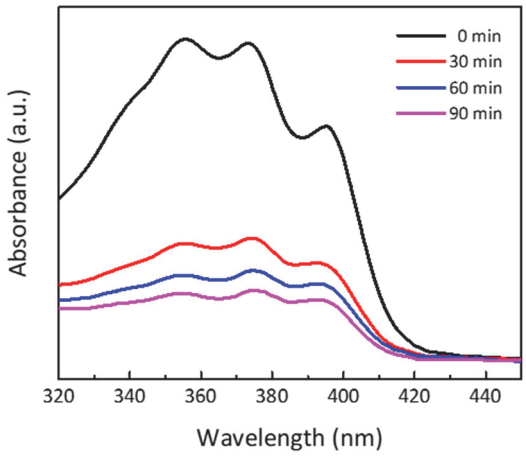
Photoluminescence decay behavior



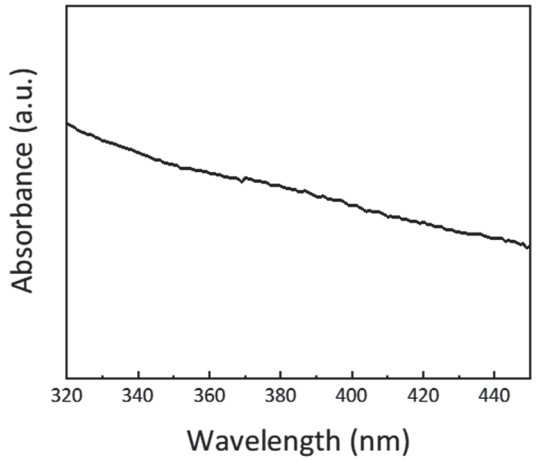
Supplementary Figure 1: Photoluminescence decay behavior of the block copolymers. (a) Time-resolved PL decay curves recorded in water and (b) histogram showing the calculated lifetimes.

UV-visible absorption spectra of PVBO homopolymer



Supplementary Figure 2: UV-visible absorption spectra of aqueous dispersions of PVBO only under UV irradiation for 90 min (recorded at 0, 30, 60, and 90 min).

UV-visible absorption spectrum of graphene_only



Supplementary Figure 3: Absorbance spectrum of the graphene colloid dispersed in water. The graphene dispersion showed no notable absorbance peak, even after UV irradiation.

Correlation between the UV/visible absorbance and the photoisomerization kinetics

Z–E photoisomerization can be described as follows:

$$(Rate) = -\frac{\Delta[Z]}{\Delta t} = k[Z] \quad \text{(S1)}$$

Integration of the above kinetic equation results in

$$\ln[Z(t)] = -kt + \ln[Z]_0 \quad \text{(S2)}$$

where $[Z(t)]$ is the concentration of the *Z* isomer at time *t*, $[Z]_0$ is the initial concentration of the *Z* isomer, and *k* is the rate constant of the reaction. Eq. S2 can be rearranged as

$$\frac{[Z(t)]}{[Z]_0} = e^{-kt} \quad \text{(S3)}$$

$$A(t) = A_{Z,t} + A_{PEO,t} + A_{Graphene,t} \quad \text{(S4)}$$

$$A_0 = A_{Z,0} + A_{PEO,0} + A_{Graphene,0} \quad \text{(S5)}$$

where the measured absorbance $A(t)$ is the sum of the components $A_{Z,t}, A_{PEO,t}$, and $A_{Graphene,t}$, which are the absorbance values of the *Z* isomer, PEO, and graphene at time *t*, respectively. By dividing $A(t)$ by the initial absorbance A_0, the following equation is obtained:

$$\frac{A(t)}{A_0} = \frac{(A_{Z,t}+A_{PEO,t}+A_{Graphene,t})}{(A_{Z,0}+A_{PEO,0}+A_{Graphene,0})} \quad \text{(S6)}$$

Letting

$$p = \frac{A_{PEO,t}}{A_{Z,0}} + \frac{A_{Graphene,t}}{A_{Z,0}} \ [\because A_{PEO,t}, A_{Graphene,t} = (constant)]$$

$$q = (1 + \frac{A_{PEO,0}}{A_{Z,0}} + \frac{A_{Graphene,0}}{A_{Z,0}})$$

and substituting *p* and *q* into Eq. S6 yields

$$\frac{A(t)}{A_0} = \frac{(A_{Z,t}/A_{Z,0}+p)}{q} \quad \text{(S7)}$$

According to the Beer–Lambert Law, Eq. S7 can be written as

$$\frac{A(t)}{A_0} = \left(\frac{1}{q}\right)\left(\frac{\varepsilon_Z l[Z(t)]}{\varepsilon_Z l[Z]_0}\right) + (\frac{p}{q}) = \left(\frac{1}{q}\right)\left(\frac{[Z(t)]}{[Z]_0}\right) + (\frac{p}{q}) \quad \text{(S8)}$$

where ε_Z is the molar absorptivity of the *Z* isomer, and *l* is the path length of the sample. Both components could be reducible.

Rearranging and substituting Eq. S3 yields the following equation.

$$\frac{[Z(t)]}{[Z]_0} = \left(q\frac{A(t)}{A_0} - p\right) = e^{-kt} \quad \text{(S9)}$$

This is rearranged as

$$\frac{A(t)}{A_0} = \frac{p}{q} + \left(\frac{1}{q}\right)e^{-kt} \quad \text{(S10)}$$

and then

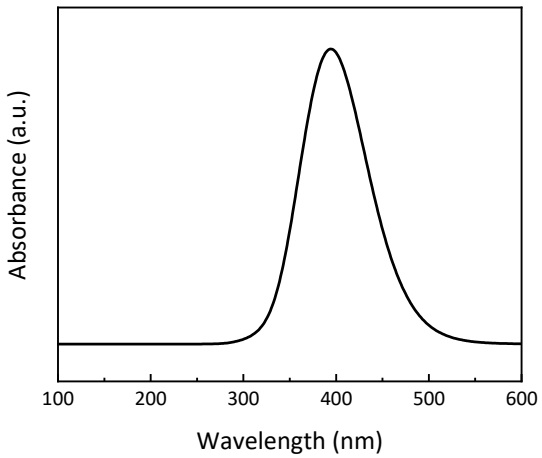
$$\alpha = \frac{A_{Z,0}}{A_{Z,0}+A_{PEO,0}+A_{Graphene,0}} = \frac{1}{q}$$

$$\beta = \frac{A_{PEO,t}+A_{Graphene,t}}{A_{Z,0}+A_{PEO,0}+A_{Graphene,0}} = \frac{p}{q}$$

are substituted into Eq. S10 to obtain

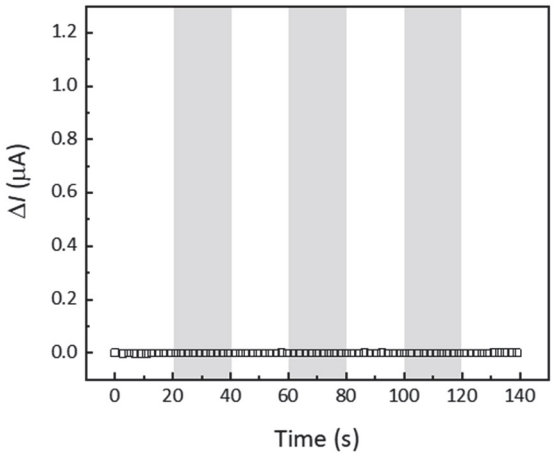
$$\frac{A(t)}{A_0} = \beta + \alpha e^{-kt} \quad \text{(S11)}$$

Time-dependent density functional theory calculation



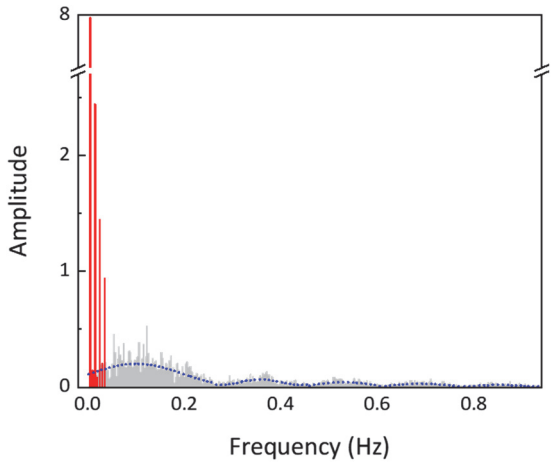
Supplementary Figure 4: UV-visible spectrum of the BO moiety obtained through time-dependent DFT calculation (B3LYP, 6-311+g(d,p), water medium, single states). A broad absorption occurred around 400 nm (max. 3.15 eV (394 nm)).

Electrical response of graphene alone



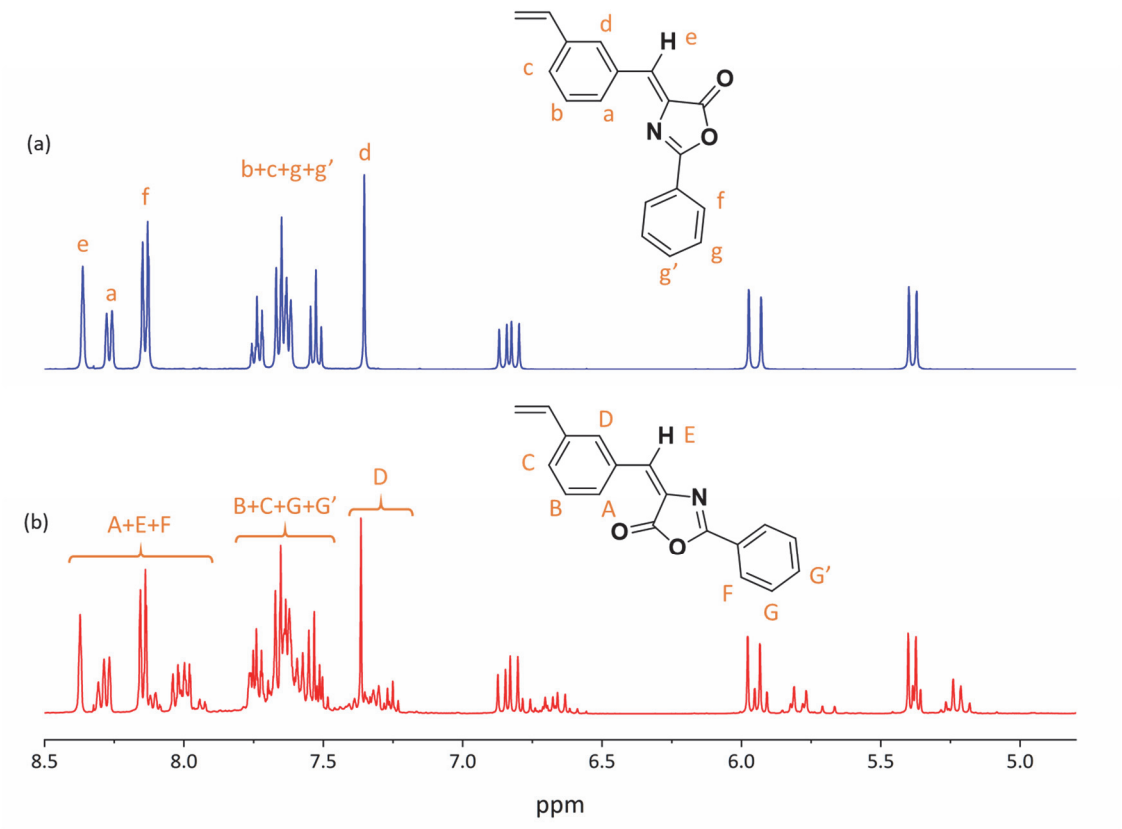
Supplementary Figure 5: Electrical response of EG recorded at an applied voltage of 0.1 V as a function of time upon periodic exposure to visible (white region) and UV (gray region) light. EG was insensitive to both types of light.

Frequency domain: two different oscillations



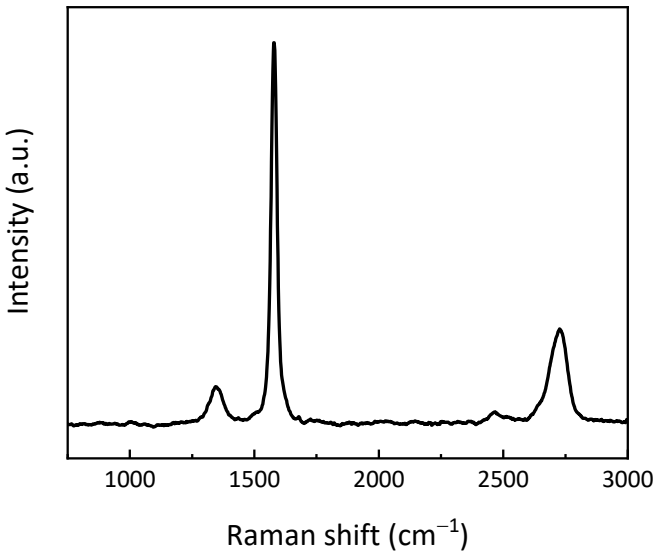
Supplementary Figure 6: Example of frequency peak f_1 (red), frequency band f_2 (blue), and their harmonics.

NMR spectra of the block copolymer isomers



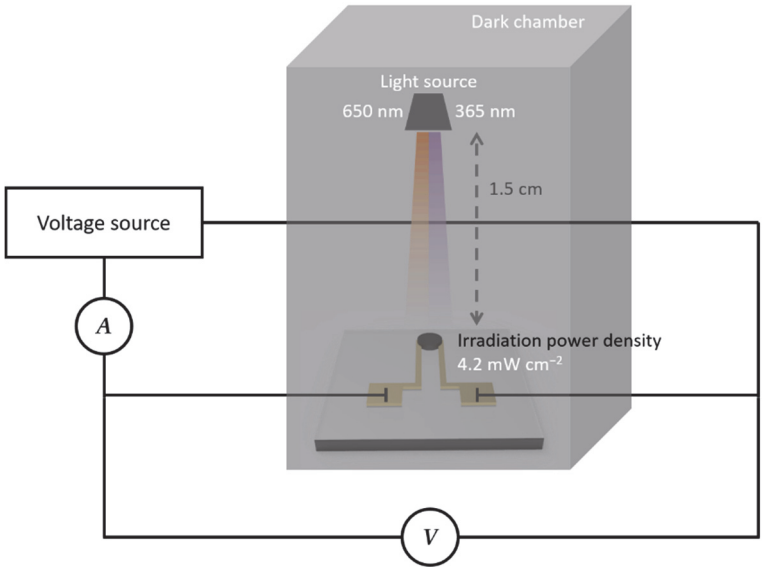
Supplementary Figure 7: Characterization of the isomers by NMR spectroscopy. ^{1}H NMR spectra of VBO measured (a) before and (b) after UV irradiation.

Characteristics of graphene precursor



Supplementary Figure 8. Raman spectrum of the graphene precursor recorded with 532.13 nm excitation using a JASCO NRS-5100 spectrophotometer. The characteristic *D*, *G*, and *G′* peaks were found at ~1340, ~1580, and ~2730 cm^{-1}. The intensity ratio of *D* peak-to-*G* peak was 0.07 and the four probe conductivity of the graphene precursor pellet was measured to be 550 S cm^{-1}.

Experimental setup for the measurement



Supplementary Figure 9. Experimental setup for the electrical monitoring of the PGNH electrode. The width of the gold finger in the used electrode was 500 μm and the inter-finger gap was 1.5 mm.