SI 1. NMR spectroscopy of compounds (7), (8), and (9)

4-(3-hexyl-5-(5-(4-hexylthiophen-2-yl)thieno[3,2-b]thiophen-2-yl)thiophen-2-yl)-N,N-bis(4-methoxyphenyl)aniline (7)
5-(5-(5-(4-(bis(4-methoxyphenyl)amino)phenyl)-4-hexylthiophen-2-yl)thieno[3,2-b]thiophen-2-yl)-3-hexylthiophene-2-carbaldehyde (8)
3-(5-(5-(4-(bis(4-methoxyphenyl)amino)phenyl)-4-hexylthiophen-2-yl)thieno[3,2-b/thiophen-2-yl)-3-hexylthiophen-2-yl)-2-cyanoacrylic acid (9)
Cyclic voltammogram of JH-1 (from ref. [15]) and JH-2 sensitizers measured at a scan rate of 100 mV/s.
SI 3. Molecules configuration and orientation

![Molecule Diagram 1 (JH-1)](image1)

\[ \text{Value 1} = -45.9462 \]
\[ \text{Value 2} = 24.4644 \]
\[ \text{Value 3} = -5.0241 \]

![Molecule Diagram 2 (PTD-02)](image2)

\[ \text{Value 4} = -48.3126 \]
\[ \text{Value 5} = -25.2148 \]
\[ \text{Value 6} = 19.1834 \]

![3D View 1 (JH-1)](image3)

![3D View 2 (PTD-02)](image4)
SI 4. Scanning Electron Microscopy images of hierarchically structured (HS-) photoelectrodes (left) and its enlarged picture showing the nanocrystalline (nc-) TiO\textsubscript{2} aggregate (right) (See ref. 18 for the details of HS-TiO\textsubscript{2} photoelectrode preparation)

SI 5. Schematic figure showing the size effect of HS TiO\textsubscript{2} and nanocrystalline (nc-) TiO\textsubscript{2} photoelectrodes.

Size effect

- (HS-TiO\textsubscript{2} Photoelectrode)
  - Fast electron transport (reduced grain boundaries)
  - Increased porosity
  - Reduced surface area
  - Resonant photoscattering

- (nc-TiO\textsubscript{2} Photoelectrode)
  - Slow electron transport (increased grain boundaries)
  - Increased surface area
  - Reduced porosity