Supporting Information

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An Efficient Narrowband Near-Infrared at 1040 nm Organic Photodetector Realized by Intermolecular Charge Transfer Mediated Coupling Based on a Squaraine Dye

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**Experimental Section**

**Materials:** All materials were purchased from commercial suppliers and used without further purification. SQ-H was prepared by the previously reported synthetic procedure.\[^{[S1]}\] Cyclic voltammetry measurements were performed on a standard commercial electrochemical analyzer (EC epsilon, BAS Instruments) in a three-electrode single-compartment cell under argon (working electrode: Pt disc, reference electrode: Ag/AgCl, and counter electrode: Pt wire). The measurements were carried out in CH\(_2\)Cl\(_2\) with a 0.1 M tetrabutylammonium hexafluorophosphate (TBAHPF) solution.

**Optical property:** UV-Vis-NIR absorption spectra were recorded by a Perkin Elmer Lambda 950 UV-Vis-NIR spectrometer equipped with an integration sphere. The SQ-H thin films were prepared by spin-coating a solution of SQ-H (2 mg mL\(^{-1}\) CHCl\(_3\)) on a quartz substrate. Thermal annealing was performed with a Gestigkeit PZ28-2 precision heating stage as indicted in the manuscript. Fluorescence spectra of annealed thin films were measured at room temperature on an Edinburgh Instruments FLS980-D2D2-ST spectrometer with a front face sample holder F-J03 (22.5°) and were corrected against the photomultiplier sensitivity and the lamp intensity. For SQ-H:PC\(_{61}\)BM BHJ thin films, the donor-acceptor blend solution of SQ-H:PC\(_{61}\)BM (1:1.5 weight ratio) in CHCl\(_3\) with a concentration of 10 mg mL\(^{-1}\) was spin-coated on quartz substrates, followed by an annealing process for 10 min at different temperatures.

**Theoretical calculations:** For estimating ground-state dipole moment and transition dipole moment, geometry optimization and time-dependent density functional theory calculation were carried out using B3LYP functional and 6-311G (d,p) basis sets as implemented Gaussian16 Package.\[^{[S2]}\] All the theoretical calculations and simulations related to the optical properties were conducted according to the previously reported methods.\[^{[S3]}\] The effective charge transfer
integrals were calculated with PW91 functional and TZP basis sets using Amsterdam Density Functional package.[S4] The nearest-neighbor dimer geometries were directly adopted from single crystal structure.

**X-ray diffraction:** Single crystal X-ray diffraction data for compound SQ-H were collected at ambient temperature (300 K) on a Bruker D8 Quest Kappa Diffractometer with a Photon100 CMOS detector and multi-layered mirror monochromated CuKα radiation. The solved structure was obtained with Fourier techniques and the Shelx software package.[S5] Crystallographic data are deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 2057832 (SQ-H). For out-of-plane XRD, SQ-H and SQ-H:PC_{61}BM (1:1.5 weight ratio) chloroform solutions (20 mg mL\(^{-1}\)) were spin-coated on zinc oxide (ZnO) deposited indium-tin oxide (ITO) substrates. And then, out-of-plane XRD were measured by a Bruker D8 Discover diffractometer with a LynxEye-1D-Detector and CuKα radiation.

**Selected area electron diffraction (SAED):** For thin-film SAED measurements, SQ-H chloroform solutions (1 mg mL\(^{-1}\)) and SQ-H:PC_{61}BM (1:1.5 weight ratio) chloroform solutions (10 mg mL\(^{-1}\)) were spin-coated on PEDOT:PSS coated glass substrates, and then thin films were annealed at different temperature for 10 min. Then the substrates were immersed in purified water and the floating thin films were transferred from water to carbon-coated copper grids (Agar Scientific Ltd., Lacey Carbon Films on 200 Mesh Copper Grids). Afterwards, the SAED measurements were carried out using a FEI Titan 80-300 transmission electron microscope with an accelerating voltage of 150 kV.
Morphology Characterization: AFM measurements were performed under ambient conditions using a Bruker Multimode 8 SPM system operating tapping mode. Silica cantilevers (OMCL-AC200TS, Olympus) with a resonance frequency of ~150 kHz and a spring constant of ~9 N m\(^{-1}\) were used. SEM images were recorded using a Carl Zeiss Ultra plus field emission scanning electron microscope equipped with GEMINI e-beam column operated at 1.5 kV with an aperture size set to 30 \(\mu\)m to avoid excessive charging and radiation damage of the areas imaged. The thin films for AFM and SEM measurement were prepared by spin-coating method (SQ-H:PC\(_{61}\)BM=1:1.5 weight ratio, 20 mg mL\(^{-1}\) in chloroform, 2000 rpm, 60 s) on the Si/SiO\(_2\) substrates.

Transistor Devices Fabrication: The SQ-H thin films were deposited on the hexamethyldisilazane (HMDS) treated Si/SiO\(_2\) substrates by spin-coating process (2 mg mL\(^{-1}\) chloroform, 5000 rpm for 30s), and then the thin films were annealed at 130 °C for 15 min. Au was deposited on the SQ-H thin films for source and drain electrodes.

Diode Devices Fabrication: Prior to fabrication ITO coated glass substrates were cleaned with detergent, and sonicated in distilled water, acetone and isopropyl alcohol for 10 min. After drying the substrates by N\(_2\) stream, UV-ozone treatment was carried out for 30 min. For the ZnO layer on the cleaned substrates, the ZnO precursor solution was prepared using a mixture of zinc acetate (400 mg), 2-methoxyethanol (4 mL), and ethanolamine (715 \(\mu\)L). Then a ZnO film was deposited by spin-coating at 2000 rpm for 60s and annealed at 150 °C for 10 min in air. Polyethylenimine (PEI, Mw = 25,000, Sigma-Aldrich) was dissolved into 2-methoxyethanol with 0.05 wt% and then PEI solution was spin-coated onto the substrates at 5000 rpm for 30s followed by an annealing process at 110 °C for 10 min in air. To form the bulk-heterojunction active layer (~ 85 nm), a blend solution of SQ-H:PC\(_{61}\)BM (1:1.5 weight ratio) in chloroform (20 mg mL\(^{-1}\)) was spin-coated on top of the ZnO layer under inert
conditions (M. Braun Inertgas Systeme GmbH; c(O₂) < 0.1 ppm, c(H₂O) < 0.1 ppm). After transferring to the OPViav-XL (Creaphys GmbH) vacuum chamber (pressure of ca. 10⁻⁷ mbar), MoO₃ (10 nm) and Ag (100 nm) electrodes were deposited on the active layer by thermal evaporation with an active area of 7.1 mm². Finally, post annealing process was carried out on a Gestigkeit PZ28-2 precision heating stage at different temperatures for 10 min. To make the hole-only diodes, 30 mg mL⁻¹ of SQ-H:PC₆₁BM (1:1.5 weight ratio) blend solution in chloroform was spin-coated on the MoO₃ (10 nm) deposited ITO substrates and then MoO₃ (10 nm) and Ag (100 nm) were subsequently deposited for the top electrode. For the electron-only diodes, the blend solution was spin-coated on the ZnO deposited ITO substrates, followed by Ca (6 nm) and Al (100 nm) thermal evaporation. Using the ITO coated polyethylene terephthalate (PET) films (Sigma-Aldrich, 639303), the flexible devices were fabricated by the same procedure as for the optimized rigid OPDs.

**Device Characterization:** The current density vs. voltage (J-V) characteristics were measured using an Agilent 4155C Semiconductor Parameter Analyzer in dark and under irradiation of monochromatic light under inert conditions (M. Braun Inertgas Systeme GmbH; c(O₂) < 0.1 ppm, c(H₂O) < 0.1 ppm). For illuminating monochromatic light, light-emitting diodes (Thorlabs, LED1050L and LED680L) with a peak wavelength of 1050 nm and 680 nm were used. The light intensity was measured by a powermeter (Newport, 2832-C) equipped with a calibrated silicon photodiode (Newport, 818-SL). The external quantum efficiency (EQE) was measured using a Newport QE/IPCE Measurement Kit comprised of a 300 W xenon lamp, a monochromator (Newport, 74125), a Merlin lock-in amplifier (Newport, 70104), an optical chopper, and a calibrated silicon photodiode (Newport, 70356_70316NS). All of the EQE were measured under a monochromatic light source modulated at 30 Hz using the optical chopper. For measurement of transient response, the LED light source (Thorlabs, LED1050L) was
modulated by a built-in waveform generator module (Agilent, DSOX2WAVEGEN) of an oscilloscope (Agilent, DSO-X 2002A) for triggering the photoresponse of OPDs. Then photoresponse signals were recorded by an oscilloscope (Agilent, DSO-X 2002A) with a 50 Ω load resistor. The noise current was directly measured by using a lock-in amplifier (Signal Recovery, 7265). For photoplethysmography (PPG) measurement, the output of the OPDs were amplified by a low noise preamplifier (PerkinElmer instruments, Model 5182) with a A/V gain factor of $10^{-7}$, and then recorded by an oscilloscope (Agilent, DSO-X 2002A) with a low-pass electrical filter (Thorlabs, EF508). The PPG was collected from one of the authors under their informed consent. No ethical approval was necessary.
Supporting Figures

Figure S1. External quantum efficiency (EQE) as function of maximum wavelength at NIR region ($\lambda_{\text{NIR, max}}$) accomplished in this work in comparison to previously reported organic dye and polymer OPDs (see also Table S1).
Figure S2. Optical properties of SQ-H thin-film. a) Normalized UV-Vis-NIR absorption and fluorescence ($\lambda_{ex} = 945$ nm) spectra of spin-coated and annealed thin-film of SQ-H on quartz. b) Change in UV-Vis-NIR absorption spectra of SQ-H on quartz recorded in-situ during annealing process with a rate of 2 K min$^{-1}$. 
Figure S3. Schematic energy diagram for squaraine dimer. $|ge_1>$ represents the optically allowed state of the non-interacting dimer, whereas $|ac_1>$ is a symmetric charge separated state (for details see Ref. S3). The symmetry is defined with regard to translation. The destabilization and stabilization of states $|ge_1>$ and $|ac_1>$, respectively, arises from Coulomb interaction between the chromophores. Accordingly, the two states are brought into resonance and are coupled leading to a splitting with two optically allowed states, which explains the two-band structure observed in the UV-Vis-NIR absorption spectrum of SQ-H in thin film.
**Figure S4.** Scaled absorption spectra of the SQ-H, PC$_{61}$BM, and bulk-heterojunction thin films thereof after thermal annealing.
Figure S5. a) Transfer and b) output characteristics of organic field-effect transistors of neat SQ-H thin films on Si/SiO₂/HDMS substrates after thermal annealing. c) The nearest-neighbor dimers along the in-plane of the SQ-H molecular packing structure (see also Table S4).
Figure S6. J-V characteristics of the a,b) hole- and c,d) electron-only SQ-H:PC61BM bulk-heterojunction devices under different annealing conditions. The SCLC mobility values are denoted in the figures. \( \mu_h \) and \( \mu_e \) represent hole and electron SCLC mobility, respectively.
Figure S7. a) TEM image of the neat SQ-H thin film annealed at 150 °C for 10 min. b-c) The corresponding SAED patterns and their respective simulation of single crystalline SQ-H domain indexed as (100), (012), and (112) planes. d) Schematic of the tilted SQ-H thin film structure. During the SAED recordings, the organic thin films (bottom left dark region in TEM image) were damaged.
Figure S8. Out-of-plane XRD patterns for the SQ-H (dark red) PC61BM (black) and their bulk-heterojunction (colored) thin films on ZnO deposited ITO substrates. The respective annealing temperatures ($T_{\text{ann}}$) are denoted in the figure.
Figure S9. SAED patterns and TEM images of polycrystalline a) neat SQ-H (annealed at 150 °C), b) BHJ with PC61BM (annealed at 50 °C), c) BHJ (annealed at 90 °C), and d) BHJ (annealed at 130 °C). e) Schematic of the two crystallites of SQ-H structure in BHJ thin films.
Figure S10. a-c) AFM height images and d-f) SEM images of the SQ-H:PC_{61}BM blend thin films on Si/SiO_{2} substrates: a,d) as-cast and annealed b,e) at 90 °C, and c,f) at 130 °C. The root-mean-square roughness (Rq) values are denoted in the Figure.

Atomic force microscopy (AFM) and scanning electron microscope (SEM) analyses were carried out to find the optimum nano-morphology for SQ-H:PC_{61}BM active layers. With the increase of annealing temperature, AFM images show smaller-scale granular structures with reduced roughness, suggesting that phase separation between donor and acceptor occurs (Figure S10 a-c). The root mean square roughness values are 5.2 ± 0.1 nm, 3.3 ± 0.1 nm, and 2.2 ± 0.1 nm for as-cast, 90 °C, and 130 °C annealing conditions, respectively. Although higher temperature annealing conditions gave a smoother surface, which is generally beneficial for BHJ OPDs, significant phase separation occurs when the annealing temperature is increased to 130 °C (Figure S10 d-e). Indeed, better EQE spectra were obtained from the OPD annealed at 90 °C compared to other annealing conditions (vide supra, Figure S11, Supporting Information).
Figure S11. External quantum efficiency (EQE) of the SQ-H:PC$_61$BM OPDs depending on the annealing temperatures of the active layer.
Figure S12. Cyclic voltammograms of a) SQ-H and b) PC₆₁BM in CH₂Cl₂ using ferrocene/ferrocnium couple as an internal standard (scan rate : 100 mV s⁻¹). The oxidation potential ($E_{1/2}$(OX))/reduction potential ($E_{1/2}$(Red)) values of SQ-H and PC₆₁BM are −0.32 V/−1.40 V and 1.18 V/−1.18 V, respectively. The HOMO and LUMO energy levels were estimated assuming a value of −5.1 eV for ferrocene.
Figure S13. a) Absorption spectrum of annealed SQ-H:PC$_{61}$BM bulk-heterojunction thin-film and LED emission spectra with maximum emission peaks at 1050 nm (gray area) and 680 nm (red area). b) $J$–$V$ curves of the OPD in the dark (black line) and under 1050 nm (gray line, ~15 mW cm$^{-2}$) and 680 nm (red line, ~15 mW cm$^{-2}$) illumination.
Figure S14. Photoresponse of the SQ-H:PC$_61$BM bulk-heterojunction OPD under the illumination of various NIR (1050 nm) light intensities. a) J-V characteristics of the SQ-H:PC$_61$BM bulk-heterojunction and b) corresponding responsivity ($R$).

Here, the responsivity ($R$) values are calculated by the following equation:

$$R = \frac{J_{ph}}{P_{light}},$$

where $J_{ph}$ is the photocurrent density [A cm$^{-2}$], which is calculated from the J-V characteristics in Figure S14a, and $P_{light}$ is the incident light intensity [W cm$^{-2}$]. The calculated $R$ value in Figure S14b agrees well with the $R$ for 1050 nm from EQE measurement (Figure S15b).
Figure S15. The spectral response of the SQ-H:PC₆₁BM bulk-heterojunction OPDs under reverse bias conditions (0 to −2 V). a) External quantum efficiency (EQE), b) responsivity (R), and c) detectivity (D*) depending on the various reverse bias conditions.
**Figure S16.** a) The calculated shot noise from the $J-V$ characteristics of the SQ-H:PC61BM BHJ OPD. b) The experimental noise spectra of the OPD at 0 V. The black, blue, and red dotted lines are calculated shot noise, thermal noise, and noise, respectively, at 0 V.

The shot noise ($i_{\text{shot}}$) and thermal noise ($i_{\text{thermal}}$) were calculated using the following equations

$$i_{\text{shot}} = \sqrt{2qI_{\text{dark}}\Delta f},$$  \hspace{1cm} (S2)

$$i_{\text{thermal}} = \frac{4k_BT\Delta f}{R_{\text{shunt}}},$$  \hspace{1cm} (S3)

where $q$ is the elementary charge, $I_{\text{dark}}$ is the dark current, $\Delta f$ is the bandwidth, $k_B$ is the Boltzmann constant, $T$ is the temperature and $R_{\text{shunt}}$ is the shunt resistance. $I_{\text{dark}}$ and $R_{\text{shunt}}$ from the $J-V$ curve are 3 nA (@ 0V) and 44.7 kΩ, respectively. Assuming that shot noise and thermal noise are dominant factors of the noise current, the noise current can be calculated by the following equation:

$$i_{\text{noise}} \approx \sqrt{(i_{\text{shot}})^2 + (i_{\text{thermal}})^2} = \sqrt{(3 \times 10^{-14})^2 + (6 \times 10^{-13})^2} = 6 \times 10^{-13} \text{ A Hz}^{-0.5}.\hspace{1cm} (S4)$$

Finally, the detectivity at 1050 nm under 0 V can be calculated by the following equation:

$$D^* = \frac{R_{\Delta f}}{i_{\text{noise}}} = \frac{0.104\times\sqrt{0.071}}{6\times10^{-13}} = 4 \times 10^{10} \text{ Jones}.\hspace{1cm} (S5)$$

Note that several previously reported papers estimated detectivity as shot-noise limited detectivity (i.e., $i_{\text{noise}} \approx i_{\text{shot}}$) without noise spectral density investigation. This approach can
overestimate detectivity by orders of magnitude. For example, our optimized OPD showed shot-noise limited detectivity of $9\times10^{11}$ Jones at 1050 nm under short-circuit condition.

To verify the calculated noise current and the detectivity values, the noise current spectral density was directly measured using a lock-in amplifier. For the frequency region between 30 Hz and 10 kHz, the noise current values were fluctuated between $1\times10^{-12}$ A Hz$^{-0.5}$ (@ 30 Hz) and $3\times10^{-13}$ A Hz$^{-0.5}$ (@ 110 Hz), see Figure S16b. Thus, the corresponding detectivity values are between $2\times10^{10}$ Jones and $9\times10^{10}$ Jones for 1050 nm, showing a similar magnitude to the calculated value ($4\times10^{10}$ Jones) from $J$-$V$ curve.
Figure S17. Phototransient response of the OPD under a) 10 kHz and b) 300 kHz modulated 1050 nm LED light at 0 V. c) Normalized photoresponse amplitude as a function of frequency. 

The RC time constant-limited cutoff frequency \( f_{RC} \) can be calculated by the following equations\(^{[S6]} \)

\[
C = \varepsilon_0 \varepsilon_r \frac{A}{d},
\]

\[
f_{RC} = \frac{1}{2\pi RC},
\]

where \( C \) is the capacitance, \( \varepsilon_0 \) is the vacuum permittivity, \( \varepsilon_r \) is dielectric constant (between 2 and 4 for typical organic semiconductors), \( A \) is the area of the active area, \( d \) is the thickness of the active layer, and \( R \) is the total series resistance of the device, which can be estimated to the sum of the series resistance of organic photodiode and the load resistance of the oscilloscope (50 \( \Omega \)). Using \( \varepsilon_0 = 8.854\times10^{-12} \text{ F m}^{-1}, \varepsilon_r = 3.5, A = 0.071 \text{ cm}^2 \text{ and } d = 85 \text{ nm}, \) the calculated \( C \) is range in 1.48 nF < \( C \) < 2.96 nF. The series resistance of our photodiode is estimated to be 40 \( \Omega \) from the \( J-V \) curve, and thus \( R \) is calculated to be 90 \( \Omega \). Therefore, \( f_{RC} \) of our organic photodiode is range in 600 kHz < \( f_{RC} \) < 1.2 Mhz.

The transit time-limited cutoff frequency \( f_{tr} \) can be calculated by the following equations\(^{[S7]} \)
\[
\mu_{\text{eff}} = \frac{2\mu_e \mu_h}{\mu_e + \mu_h}, \quad (S8)
\]
\[
f_{tr} = \frac{3.5}{2\pi \tau_{tr}} = \frac{3.5 \mu_{\text{eff}} (V + V_{bi})}{2\pi d^2}, \quad (S9)
\]
where \(\mu_{\text{eff}}\) is the effective carrier mobility, \(\mu_e\) is the electron mobility, \(\mu_h\) is the hole mobility, \(\tau_{tr}\) is the transit time of the charge carriers, \(V\) is the applied bias, \(V_{bi}\) is the built-in voltage, \(d\) is the thickness of the active layer. Using the SCLC mobilities (\(\mu_e = 2 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\) and \(\mu_h = 1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\)), \(\mu_{\text{eff}}\) is calculated to be \(4 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\). In other words, effective carrier mobility is governed by relatively low electron mobility of \(\text{PC_{61}BM}\). Accordingly, \(f_{tr}\) is calculated to be 330 kHz, which is close to the experimental result (300 kHz).

Therefore, we assume that cutoff frequency of \textbf{SQ-H OPD} (300 kHz) is limited by \(f_{tr}\) (330 kHz) rather than \(f_{RC}\) (600 kHz < \(f_{RC}\) < 1.2 MHz).
Figure S18. Flexible OPD characteristics. a) $J$–$V$ curves of the OPD in the dark and under illumination with NIR light (~3 mW cm$^{-2}$ @ 1050 nm). b) EQE and responsivity spectrum under 0 V.
Table S1. The references of the NIR OPDs devices in the Figure S1 with full-width at half-maximum (FWHM) values.

| #  | Active layer(a)                  | λ_{NIR,max} [nm](b) | EQE [%](c) | FWHM [nm](d) | Reverse bias [V] | Active Area [mm²](d) | Ref.                  |
|----|--------------------------------|---------------------|------------|---------------|-----------------|------------------------|-----------------------|
| 1  | SQ-H:PC<sub>61</sub>BM          | 1050                | 12.3       | 85            | 0               | 7.1                    | This work             |
| 2  | SQ-H:PC<sub>61</sub>BM          | 1050                | 20.5       | 91            | −1              | 7.1                    | This work             |
| 3  | SQ-H:PC<sub>61</sub>BM          | 1050                | 24.1       | >200          | −2              | 7.1                    | This work             |
| 4  | DTBPh:C<sub>60</sub>            | 1045                | 1.2        | >200          | 0               | -                      | [S8]                  |
| 5  | CNPh:C<sub>60</sub>             | 1130                | 1.6        | >200          | 0               | -                      | [S8]                  |
| 6  | Psub:C<sub>60</sub>             | 1090                | 2.1        | >200          | 0               | -                      | [S8]                  |
| 7  | Pfused:C<sub>60</sub>           | 1350                | 6.5        | >250          | 0               | -                      | [S8]                  |
| 8  | Psub: C<sub>60</sub>            | 1150                | 3.6        | >200          | 0               | -                      | [S9]                  |
| 9  | Pfused: C<sub>60</sub>          | 1400                | 10.5       | >200          | 0               | -                      | [S9]                  |
| 10 | Heptamethine salt cation 1*BF<sub>4</sub>−: C<sub>60</sub> | 1200 | 2.1 | >500 | 0 | 5.7 | [S10] |
| 11 | Heptamethine salt cation 1*TPFB−: C<sub>60</sub> | 1200 | 1.1 | >500 | 0 | 5.7 | [S10] |
| 12 | Heptamethine salt cation 2*BF<sub>4</sub>−: C<sub>60</sub> | 1350 | 1.4 | >500 | 0 | 5.7 | [S10] |
| 13 | Heptamethine salt cation 2*TPFB−: C<sub>60</sub> | 1350 | 0.8 | >500 | 0 | 5.7 | [S10] |
| 14 | P3:PC<sub>71</sub>BM            | 1100                | 7          | >500          | 0               | 9.0                    | [S11]                 |
| 15 | P4: PC<sub>71</sub>BM           | 1200                | 6          | >500          | 0               | 9.0                    | [S11]                 |
| 16 | P5: PC<sub>71</sub>BM           | 1350                | −1         | >500          | 0               | 9.0                    | [S11]                 |
| 17 | P1(P4 of ref.[5]):PC<sub>71</sub>BM | 1100 | 17 | >300 | 0 | 9.0 | [S12] |
| 18 | P1(P4 of ref.[5]): PC<sub>71</sub>BM +Camphoric anhydride | 1100 | 26 | >300 | 0 | 9.0 | [S12] |
| 19 | P2:PC<sub>71</sub>BM            | 1100                | 3.8        | >300          | 0               | 9.0                    | [S12]                 |
| 20 | P2:PC<sub>71</sub>BM +Camphoric anhydride | 1100 | 7.8 | >300 | 0 | 9.0 | [S12] |
| 21 | PBBTPD:Tri-PC<sub>69</sub>BM     | 1200                | −16        | >500          | −0.5            | 4.5                    | [S13]                 |
| 22 | DPP-DTT:SWIR dye                | 1100                | −0.45      | >300          | −0.05           | 10&150                 | [S14]                 |
| 23 | PTTQ(BO):PC<sub>71</sub>BM       | 1145                | −18        | >400          | −2              | 3                      | [S15]                 |
| 24 | PTTQ(BO):PC<sub>71</sub>BM       | 1145                | −10        | >400          | 0               | 3                      | [S15]                 |
| 25 | PTTQ(HD):PC<sub>71</sub>BM       | 1117                | −6         | >400          | −2              | 3                      | [S15]                 |
|   | Compound         | Number | λ (nm) | FWHM (nm) | Width (nm) | EQE (%) | Ref. |
|---|------------------|--------|--------|-----------|------------|---------|------|
| 26| PTTQ(HD):PC$_7$BM| 1117   | ~4     | >400      | 0          | 3       | [S15]|
| 27| PTTQ(OD):PC$_7$BM| 1053   | ~8     | >400      | −2         | 3       | [S15]|
| 28| PTTQ(OD):PC$_7$BM| 1053   | ~6     | >400      | 0          | 3       | [S15]|
| 29| PBTTQ(HD):PC$_7$BM| 1015   | ~12    | >300      | −2         | 3       | [S15]|
| 30| PBTTQ(HD):PC$_7$BM| 1035   | ~5     | >300      | 0          | 3       | [S15]|
| 31| PBTTQ(OD):PC$_7$BM| 1018   | ~7     | >300      | −2         | 3       | [S15]|
| 32| PBTTQ(OD):PC$_7$BM| 1018   | ~6     | >300      | 0          | 3       | [S15]|

*a) NIR absorbing components are highlighted in bold; b,c,d) Several values are estimated from reported EQE or responsivity spectra.
Table S2. Parameters for modeling the absorption spectra of SQ-H in Figure 3.

| Parameter | Definition | Values | Monomer | Dimer |
|-----------|------------|--------|---------|-------|
| $\eta_Z$  | Energy difference between neutral and zwitterionic state | | 1560 cm$^{-1}$ | 1560 cm$^{-1}$ |
| $t_Z$     | Electronic coupling between neutral and zwitterionic state | | 7430 cm$^{-1}$ | 7430 cm$^{-1}$ |
| $\omega_\nu$ | Vibrational frequency | | 1300 cm$^{-1}$ | 1300 cm$^{-1}$ |
| $v_{ib_{\text{max}}}$ | Maximal number of total vibrational quanta for each chromophore | | 6 | 6 |
| $\lambda_\nu^Z$ | Huang-Rhys factor for zwitterionic state | | 0.86 | 0.86 |
| $\eta_{\text{CT}}$ | Energy difference between neutral and intermolecular charge transfer (CT) state | | – | 7800 cm$^{-1}$ |
| $t_{\text{CT}}$ | Electronic coupling between neutral and intermolecular CT state | | – | 4300 cm$^{-1}$ |
| $\lambda_\nu^{CT}$ | Huang-Rhys factor for intermolecular CT state | | – | 0.36 |
| $\epsilon_r$ | Screening factor for Coulomb interaction | | – | 2.9 |
| $\Delta E$ | Overall spectral shift arising from polarizable surroundings | | – | –850 cm$^{-1}$ |
| $\sigma$ | Full width at 1/$\epsilon$ height of absorbance | | 350 cm$^{-1}$ | 350 cm$^{-1}$ |
Table S3. Summary of optical properties of SQ-H in CH₃Cl₂ solution and their spin-coated neat and BHJ (SQ-H:PC₆1BM=1:1.5 weight ratio) thin films on quartz substrates.

|                | λ_{Abs.peak1} | FWHM_{peak1} | λ_{Abs.peak2} | FWHM_{peak2} | λ_{PL} | FWHM_{PL} | Δṽ_{Stokes} |
|----------------|---------------|--------------|---------------|--------------|--------|-----------|-------------|
|                | [nm]          | [nm/cm⁻¹]    | [nm]          | [nm/cm⁻¹]    | [nm]   | [nm/cm⁻¹] | [nm/cm⁻¹]   |
| Solution       | 870           | 44/584       | –             | –            | –      | –         | –           |
| As-cast thin-film | 799           | –            | 909           | 327/3278     | –      | –         | –           |
| Annealed thin-film | 688           | 65/1335      | 1040          | 59/555       | 1050   | 44/400    | 10/90       |
| Annealed BHJ thin-film | 688           | 73/1496      | 1040          | 71/676       | –      | –         | –           |

a) Absorption peaks in absorption spectrum and b) corresponding full width at half maximum; c) Maximum emission peak in photoluminescence spectrum and d) corresponding full width at half maximum; e) Stokes shift.
Table S4. The charge transfer integral values for hole ($t_h$) and electron ($t_e$) carriers of the nearest-neighbor dimers

| Dimer $^a$ | $t_h$ [meV] $^b$ | $t_e$ [meV] $^c$ |
|------------|------------------|------------------|
| D1         | 253              | −93              |
| D2         | 8                | 0                |
| D3         | −20              | 0                |

$^a$) The nearest-neighbor dimers in SQ-H single crystal structure (Figure S5c); $^b,c$) Charge transfer integral values were calculated using PW91 functional and TZP basis sets implemented Amsterdam Density Functional package.
Table S5. The characteristics of the SQ-H:PC_{61}BM-based bulk-heterojunction OPDs with various reverse bias conditions.

| Reverse Bias [V] | EQE@690 nm [%] | R@690 nm [A W^{-1}] | D*@690 nm [Jones] | EQE@1050 nm [%] | R@1050 nm [A W^{-1}] | D*@1050 nm [Jones] |
|------------------|----------------|----------------------|-------------------|----------------|----------------------|-------------------|
| 0                | 13.07          | 0.073                | 3.22×10^{-10}     | 12.26          | 0.104                | 4.59×10^{-10}     |
| 0.01             | 13.24          | 0.074                | 2.90×10^{-10}     | 12.55          | 0.106                | 4.18×10^{-10}     |
| 0.02             | 13.57          | 0.075                | 2.71×10^{-10}     | 12.85          | 0.109                | 3.91×10^{-10}     |
| 0.1              | 14.96          | 0.083                | 2.07×10^{-10}     | 14.17          | 0.120                | 2.99×10^{-10}     |
| 0.5              | 18.75          | 0.104                | 1.30×10^{-10}     | 17.78          | 0.151                | 1.88×10^{-10}     |
| 1                | 21.36          | 0.119                | 9.50×10^{-9}      | 20.45          | 0.173                | 1.38×10^{-9}      |
| 2                | 24.51          | 0.136                | 5.96×10^{-9}      | 24.08          | 0.204                | 8.91×10^{-9}      |
**Table S6. Crystal data and structure refinement for SQ-H.**

| Compounds                        | SQ-H                                      |
|----------------------------------|-------------------------------------------|
| CCDC number                      | 2057832                                   |
| Chemical formula                 | C_{51}H_{64}N_{4}O                        |
| $M$ / g mol$^{-1}$               | 749.06                                    |
| $T$ / K                          | 300                                       |
| Crystal description              | plate                                     |
| Crystal color                    | green                                     |
| Crystal system                   | Monoclinic                                |
| Space group                      | P 2/c                                     |
| $a$ / Å                          | 6.6946(3)                                 |
| $b$ / Å                          | 9.6069(5)                                 |
| $c$ / Å                          | 34.7009(16)                               |
| $\alpha$ / °                     | 90                                        |
| $\beta$ / °                      | 90.215(4)                                 |
| $\gamma$ / °                     | 90                                        |
| $V$ / Å³                         | 2231.75(18)                               |
| $Z$                              | 2                                         |
| $\rho_{cal}$ / g cm$^{-3}$       | 1.115                                     |
| $\mu$ / mm$^{-1}$                | 0.504                                     |
| $F(000)$                         | 812                                       |
| Measurement range of $\theta$ / °| 2.547-75.254                              |
| Completeness / %                 | 99.9                                      |
| Number of independent reflections| 4569                                      |
| Parameters/restraints            | 256/0                                     |
| Goodness of fit for $F^2$        | 1.039                                     |
| $R_I > 2\sigma(I)$               | $R_I = 0.0522; \mu R_2 = 0.1382$          |
| $R$ (all data)                   | $R_I = 0.0753; \mu R_2 = 0.1555$          |
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