Supplementary Information for

A photochemical layer-by-layer solution process for preparing organic semiconducting thin films having the right material at the right place

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## Contents

1. Photoreaction monitoring ........................................................................................................ S2
   1.1. PhBADTDK to PhBADT ........................................................................................................ S2
   1.2. AtDDK to AtD .................................................................................................................... S3
2. Computation ............................................................................................................................... S4
   2.1. Method ............................................................................................................................... S4
   2.2. Full citation of Gaussian 09 ............................................................................................. S5
   2.3. Frontier-orbital energies of AtD ......................................................................................... S5
   2.4. Molecular conformation ..................................................................................................... S6
3. Device fabrication and optimization ......................................................................................... S6
   3.1. General .............................................................................................................................. S6
   3.2. Optimization of the active layer ........................................................................................ S7
       3.2.1. Material ratio in the i-layer of p–i–n devices ............................................................... S7
       3.2.2. p-Layer material .......................................................................................................... S8
       3.2.3. Annealing conditions .................................................................................................. S8
       3.2.4. Comparison of cathode buffers ................................................................................ S10
   3.3. Estimation of the material composition in the optimized p–i–n-type active layer ........ S11
   3.4. Stability of PC_{71}BM under the irradiation in the photoprecursor approach ........... S12
4. Chemical synthesis .................................................................................................................... S12
   4.1. General .............................................................................................................................. S12
   4.2. Materials .......................................................................................................................... S13
   4.3. Synthesis of PhBADTDK .................................................................................................. S13
   4.4. Synthesis of AtDDK ......................................................................................................... S16
5. NMR spectra ............................................................................................................................. S21
6. References ................................................................................................................................ S31
1. Photoreaction monitoring

The photoreactions of PhBADTDK and AtDDK in solution were monitored via UV–Vis absorption and $^1$H NMR measurements as follows: For UV–Vis absorption measurements, sample solutions were prepared by dissolving approximately 0.2 mg of a photoprecursor in 10 mL of toluene. Each solution was transferred to a quartz cuvette and deoxygenated by argon bubbling for at least 30 min. UV–Vis absorption was measured periodically during irradiation with a blue LED lamp ($\lambda = 470 \pm 10$ nm). For the monitoring by $^1$H NMR, approximately 1 mg of a photoprecursor was dissolved in 0.5 mL of CDCl$_3$ in an NMR tube equipped with a J. Young valve. The solution was degassed by three freeze–pump–thaw cycles, and the tube was refilled with argon. The solution was irradiated with a metal halide lamp through a blue cut filter, and periodically subjected to $^1$H NMR measurement.

The progress of the photoreactions in thin films was confirmed by IR spectroscopy. Sample films were prepared by spin-coating of a 10 mg mL$^{-1}$ solution of each photoprecursor in CHCl$_3$ on glass/ITO substrate at 800 rpm for 30 s. IR spectra were measured before and after irradiation with a blue LED lamp ($\lambda = 470 \pm 10$ nm) at an intensity of 0.5 W cm$^{-2}$ for 30 min. The irradiation was performed in a nitrogen-filled glove box.

1.1. PhBADTDK to PhBADT

The spectroscopic changes upon photoirradiation of PhBADTDK are summarized in Fig. S1. The change in UV–Vis absorption during an early stage of the reaction in toluene was associated with isosbestic points at 317 and 438 nm, indicating that the stoichiometry of reaction remained unchanged, and thus the reaction to PhBADT proceeded without side reactions (Fig. S1b). Note that extended irradiation resulted in the formation of a yellow precipitate, most likely of PhBADT. The clean conversion of PhBADTDK to PhBADT in solution was confirmed by $^1$H NMR; namely, the spectrum after photoirradiation for 60 s showed complete consumption of PhBADTDK (evident from disappearance of the bridgehead proton H$^a$ at 5.4 ppm), and the newly appeared peaks were fully consistent with PhBADT, including the characteristic singlet at 8.7 ppm that could be assigned to H$^b$ (Fig. S1a, c). The IR spectra of thin films clearly showed disappearance of the carbonyl groups upon photoirradiation, indicating that the intended photoreaction proceeded effectively even in the thin-film state (Fig. S1d).
Fig. S1 Spectroscopic change in the photoreaction of PhBADTDK to PhBADT. (a) Reaction scheme highlighting the protons that give characteristic $^1$H NMR signals; (b) Change in UV–Vis absorption during an early stage of the reaction in toluene; (c) $^1$H NMR spectra before and after photoirradiation with a metal-halide lamp for 60 s in CDCl$_3$; (d) IR spectra of thin films before and after photoirradiation with a blue LED for 30 min.

1.2. AtDDK to AtD

The spectroscopic changes upon photoirradiation of AtDDK are summarized in Fig. S2. The change in UV–Vis absorption during an early stage of the reaction in toluene was associated with isosbestic points at 445 and 590 nm, indicating that the stoichiometry of the reaction remained unchanged, and thus the photoreaction proceeded without side reactions (Fig. S2b). The absorption edge redshifted along with the progress of the photoreaction, which was consistent with the elongation of $\pi$-conjugation upon the intended decarbonylative aromatization. Note that extended irradiation led to the formation of a dark blue precipitate, most likely of AtD. As shown in Fig. S2c, the $^1$H NMR signals of AtDDK completely disappeared after photoirradiation with a metal halide light for 150 min. In contrast to the case of PhBADTDK, no signals of the product was detected.
after the disappearance of the photoprecursor, indicating the extremely low solubility of the product in chloroform. The IR spectra of thin films showed disappearance of the α-diketone groups upon photoirradiation, strongly supporting the effective progress of the intended photoreaction in the thin-film state (Fig. S2d). At the same time, the amide carbonyl of DTDPP unit (ca. 1670 cm⁻¹) remained after the photoirradiation.

![reaction_diagram](attachment:reaction.png)

**Fig. S2** Spectroscopic change in the photoreaction of AtDDK to AtD. (a) Reaction scheme; (b) Change in UV–Vis absorption during an early stage of the reaction in toluene; (c) ¹H NMR spectra before and after photoirradiation with a metal-halide lamp for 150 min in CDCl₃; (d) IR spectra of thin films before and after photoirradiation with a blue LED for 30 min.

### 2. Computation

#### 2.1. Method

All calculations were performed using the B3LYP method implemented in *Gaussian 09*, full citation of which is shown in the next section. Geometry optimizations were performed using the 6-31G(d) basis set with
tight convergence criteria and no symmetry constraints. Vibrational frequencies were computed for all optimized structures to verify that these structures were minima. The two 2-ethylhexyl groups of AtD were replaced with methyl groups in the calculations in order for saving calculation time.

2.2. Full citation of Gaussian 09

*Gaussian 09*, Revision E.01: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

2.3 Frontier-orbital energies of AtD

![Graph showing frontier-orbital energies](image)

*Fig. S3* Frontier-orbital energies of AtD and its building components At and DTDPP calculated at the B3LYP/6-31G(d) level of theory. The 2-ethylhexyl groups are replaced with methyl groups for saving the calculation time.
2.4. Molecular conformation

Fig. S4 Molecular structures optimized at the B3LYP/6-31G(d) level of theory: (a) PhBADT; (b) AtD. The 2-ethylhexyl groups are replaced with methyl groups for saving the calculation time.

3. Device fabrication and evaluation

3.1. General

Indium-tin-oxide (ITO)-patterned glass substrates (20 × 25 mm², 15 ohm per square) were cleaned by gentle rubbing with an acetone-soaked wipe for ca. 5 s, sonication in acetone and isopropanol for 10 min each, and exposure to boiling isopropanol for 10 min. The washed substrates were further treated in a UV–O₃ cleaner (Filgen, UV253V8) for 20 min, before the poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) layer (PEDOT:PSS, Clevios P VP AI4083) was deposited by spin-coating at 5000 rpm for 40 s followed by thermal annealing at 120 °C for 20 min in air. The thickness of the resulting PEDOT:PSS layer was about 30 nm. The substrates were then transferred to a N₂-filled glove box (<0.5 ppm O₂ and H₂O) for preparation of the organic layers. After deposition of the organic active layers, the calcium or ETL-1 buffer and then the aluminum electrode were deposited. In the case of calcium buffer, calcium (10 nm) and aluminum (80 nm) were sequentially vapor-deposited at high vacuum (~10⁻⁵ Pa) through a shadow mask that defined an active area of 2.0 × 2.0 mm². In the case of ETL-1 buffer, ETL-1 was spin-coated from a 0.5 mg mL⁻¹ solution in methanol at 800 rpm for 30 s, and then aluminum (80 nm) was deposited at high vacuum (~10⁻⁵ Pa) through the same shadow mask as in the case of calcium buffer. ETL-1 was found to afford slightly higher photovoltaic performance (Table S8), and thus used in all the devices shown in Table 1 in the main text. On the other hand, calcium was used only in the early stage of the optimization process described in this Supplementary Information.
3.2. Optimization of the active layer

3.2.1. Material ratio in the i-layer of p–i–n devices

Three different p:n ratios (2:1, 1:1 and 1:2 by weight) were tried for the i-layer in p–i–n-type devices having a general structure of [ITO/PEDOT:PSS/DTA/AtD:PC\textsubscript{71}BM/PC\textsubscript{71}BM/Ca/Al]. DTA and AtD:PC\textsubscript{71}BM were deposited by spin-coating of DTADK (5 mg mL\textsuperscript{-1} in CHCl\textsubscript{3}) and AtDDK:PC\textsubscript{71}BM (10 mg mL\textsuperscript{-1}), respectively, at 800 rpm for 30 s, followed by irradiation with a blue LED (470 ± 10 nm) at 0.5 W cm\textsuperscript{-2} for 30 min. PC\textsubscript{71}BM were spin-coated from a 5 mg mL\textsuperscript{-1} solution in CHCl\textsubscript{3} at 800 rpm for 30 s. This device structure was adopted from our preliminary work in which the i-layer was a 2:1 (by weight) blend of EH-DBTA and PC\textsubscript{71}BM (see Fig. S5 for chemical structures of DTA, EH-DBTA and their \(\alpha\)-diketone-type photoprecursors).\textsuperscript{51}

Note that the p:n weight ratios are defined as the ratio between a photoprecursor and PC\textsubscript{71}BM. Among the tested ratios, 1:1 was found the best (Table S1) and used in all the following experiments.

![Fig. S5 Chemical structures of DTA, EH-DBTA and their photoprecursors.](image)

Table S1 Performance of p–i–n OPVs having i-layers of different p:n ratios.\textsuperscript{a,b}

| Entry | p:n ratio\textsuperscript{a} | \(J_{SC}\) (mA cm\textsuperscript{-2}) | \(V_{OC}\) (V) | FF (%) | PCE (%) | \(R_s\) (\(\Omega\) cm\textsuperscript{2}) | \(R_p\) (\(\Omega\) cm\textsuperscript{2}) |
|-------|-----------------|----------------|----------------|--------|--------|----------------|----------------|
| S1    | 2:1             | 7.24           | 0.89           | 36.0   | 2.3    | 50             | 265            |
| S2    | 1:1             | 7.95           | 0.88           | 45.0   | 3.2    | 24             | 420            |
| S3    | 1:2             | 7.59           | 0.87           | 43.8   | 2.9    | 32             | 417            |

\textsuperscript{a}Data of the best-performing devices. \textsuperscript{b}General device structure: [ITO/PEDOT:PSS (30 nm)/DTA (5 mg mL\textsuperscript{-1} in CHCl\textsubscript{3})/AtD:PC\textsubscript{71}BM in different ratios (10 mg mL\textsuperscript{-1} in CHCl\textsubscript{3})/PC\textsubscript{71}BM (5 mg mL\textsuperscript{-1} in CHCl\textsubscript{3})/Ca (10 nm)/Al (80 nm)]. The concentrations are of the cast solutions.

\textsuperscript{c}Defined as the weight ratio between the photoprecursor AtDDK and PC\textsubscript{71}BM.
3.2.2. p-Layer material

PhBADT was compared with DTA as p-layer material in p-i-n devices having a general structure of [ITO/PEDOT:PSS/p-layer/AtD:PC71BM/PC71BM/ETL-1/Al]. The p-layer was deposited by spin-coating of PhBADTDK or DTADK (5 mg mL⁻¹ in CHCl₃) at 800 rpm for 30 s, followed by irradiation with a blue LED (470 ± 10 nm) at 0.5 W cm⁻² for 30 min. The i-layer was prepared by spin-coating of AtDDK:PC71BM (1:1 by weight, 10 mg mL⁻¹ in CHCl₃) followed by irradiation with a blue LED at 1 W cm⁻² for 30 min. PC71BM and ETL-1 were spin-coated from a 5 mg mL⁻¹ solution in CHCl₃ and a 0.5 mg mL⁻¹ solution in MeOH, respectively, at 800 rpm for 30 s. As shown in Table S2, PhBADT gave a higher $J_{SC}$ and FF as compared to DTA under the examined conditions.

**Table S2** Performance of p-i-n OPVs having DTA or PhBADT as p-layer material.$^{a,b}$

| Entry | p-layer | $J_{SC}$ (mA cm⁻²) | $V_{OC}$ (V) | FF (%) | PCE (%) | $R_s$ (Ω cm²) | $R_p$ (Ω cm²) |
|-------|---------|--------------------|------------|-------|--------|-------------|-------------|
| S4    | DTA     | 9.92               | 0.89       | 47.5  | 4.2    | 17          | 369         |
| S5    | PhBADT  | 10.28              | 0.88       | 52.7  | 4.8    | 11          | 470         |

$a$ Data of the best-performing devices. $b$ General device structure: [ITO/PEDOT:PSS (30 nm)/p-layer (5 mg mL⁻¹ in CHCl₃)/AtD:PC71BM (1:1 by weight, 10 mg mL⁻¹ in CHCl₃)/PC71BM (5 mg mL⁻¹ in CHCl₃)/ETL-1 (0.5 mg mL⁻¹ in MeOH)/Al (80 nm)]. The concentrations are of the cast solutions.

3.2.3. Annealing conditions

Annealing of bulk-heterojunction active layers. AtD:PC71BM (1:1) bulk-heterojunction (BHJ) layers were exposed to solvent vapor (CHCl₃, CS₂, or tetrahydrofuran (THF)) for 60 s, and photovoltaic performance of the resulting films was measured in devices with a general configuration of [ITO/PEDOT:PSS/AtD:PC71BM/ETL-1/Al]. The BHJ layer was prepared by spin-coating of a AtDDK:PC71BM (1:1 by weight, 10 mg mL⁻¹ in CHCl₃) followed by irradiation with a blue LED (470 ± 10 nm) at 0.5 W cm⁻² for 30 min. ETL-1 was spin-coated from a 0.5 mg mL⁻¹ solution in MeOH at 800 rpm for 30 s. While the solvent-vapor annealing (SVA) led to significantly improved photovoltaic performance in all the three cases, THF was found the most effective (Table S3).
Table S3 Performance of BHJ OPVs subjected to SVA for 60 s.\textsuperscript{a,b}

| Entry | Annealing solvent | $J_{sc}$ (mA cm$^{-2}$) | $V_{oc}$ (V) | FF (%) | PCE (%) | $R_1$ (Ω cm$^2$) | $R_0$ (Ω cm$^2$) |
|-------|-------------------|-------------------------|-------------|--------|--------|----------------|----------------|
| S6    | – (as cast)       | 2.68                    | 0.91        | 24.5   | 0.60   | 224            | 316            |
| S7    | CHCl$_3$          | 7.64                    | 0.90        | 39.9   | 2.7    | 30             | 306            |
| S8    | CS$_2$            | 7.80                    | 0.91        | 39.3   | 2.8    | 31             | 302            |
| S9    | THF               | 7.74                    | 0.89        | 43.1   | 3.0    | 22             | 361            |

\textsuperscript{a}Data of the best-performing devices. \textsuperscript{b}General device structure: [ITO/PEDOT:PSS (30 nm)/AtD:PC$_{71}$BM (1:1 wt, 10 mg mL$^{-1}$ in CHCl$_3$)/ETL-1 (0.5 mg mL$^{-1}$ in MeOH)/Al (80 nm)]. The concentrations are of the cast solutions.

Two other common techniques for morphology improvement, namely thermal annealing and the use of high-boiling-point additive, were also examined for the OPVs having the same device configuration as above except that calcium was used instead of ETL-1 as cathode buffer. However, these treatments were found to be essentially ineffective to the AtD:PC$_{71}$BM system (Tables S4 and S5), and thus not pursued further.

Table S4 Performance of BHJ OPVs prepared with thermal annealing.\textsuperscript{a-c}

| Entry | Annealing temperature | $J_{sc}$ (mA cm$^{-2}$) | $V_{oc}$ (V) | FF (%) | PCE (%) | $R_1$ (Ω cm$^2$) | $R_0$ (Ω cm$^2$) |
|-------|-----------------------|-------------------------|-------------|--------|--------|----------------|----------------|
| S10   | – (as cast)           | 2.19                    | 0.88        | 24.0   | 0.46   | 275            | 357            |
| S11   | 100 °C                | 2.04                    | 0.88        | 23.7   | 0.43   | 311            | 378            |
| S12   | 150 °C                | 1.96                    | 0.9         | 23.3   | 0.41   | 371            | 396            |

\textsuperscript{a}Data of the best-performing devices. \textsuperscript{b}General device structure: [ITO/PEDOT:PSS (30 nm)/AtD:PC$_{71}$BM (1:1 wt, 10 mg mL$^{-1}$ in CHCl$_3$)/Ca (10 nm)/Al (80 nm)]. The concentration is of the cast solution. \textsuperscript{c}Annealing duration was 10 min.

Table S5 Performance of BHJ OPVs prepared by using o-dichlorobenzene as additive in cast solutions.\textsuperscript{a-c}

| Entry | Additive content\textsuperscript{a} | $J_{sc}$ (mA cm$^{-2}$) | $V_{oc}$ (V) | FF (%) | PCE (%) | $R_1$ (Ω cm$^2$) | $R_0$ (Ω cm$^2$) |
|-------|-------------------------------------|-------------------------|-------------|--------|--------|----------------|----------------|
| S13   | – (no additive)                     | 2.09                    | 0.86        | 23.8   | 0.43   | 387            | 366            |
| S14   | 0.5%                                | 1.95                    | 0.90        | 23.7   | 0.42   | 403            | 404            |
| S15   | 1%                                  | 2.12                    | 0.90        | 24.1   | 0.46   | 254            | 393            |
| S16   | 2%                                  | 2.01                    | 0.69        | 24.3   | 0.33   | 72             | 329            |

\textsuperscript{a}Data of the best-performing devices. \textsuperscript{b}General device structure: [ITO/PEDOT:PSS (30 nm)/AtD:PC$_{71}$BM (1:1 wt, 10 mg mL$^{-1}$ in CHCl$_3$)/Ca (10 nm)/Al (80 nm)]. The concentration is of the cast solutions. \textsuperscript{c}Volume percent in the cast solvent.

**Annealing of p–i–n active layers.** The optimal timing and duration of THF SVA were examined for the p–i–n OPV having a configuration of [ITO/PEDOT:PSS/PhBADT/AtD:PC$_{71}$BM/PC$_{71}$BM/ETL-1/Al]. PhBADT was deposited by spin-coating of PhBADTDK (1 mg mL$^{-1}$ in CHCl$_3$) at 800 rpm for 30 s, followed by irradiation with a blue LED (470 ± 10 nm) at 0.5 W cm$^{-2}$ for 10 min. The i-layer was prepared by spin-coating of AtDDK:PC$_{71}$BM (1:1 by weight, 8 mg mL$^{-1}$ for entries S17 and S18, 9 mg mL$^{-1}$ for entries S19–
S23 in CHCl$_3$) followed by irradiation with a blue LED at 1 W cm$^{-2}$ for 30 min. PC$_{71}$BM and ETL-1 were spin-coated from a 5 mg mL$^{-1}$ solution in CHCl$_3$ and a 0.5 mg mL$^{-1}$ solution in MeOH, respectively, at 800 rpm for 30 s. The results show that the SVA treatment would be better performed after the deposition of the i-layer rather than n-layer (Table S6). The optimal duration was determined to be 120 s, although the difference in photovoltaic performance was only marginal within 60–180 s (Table S7).

### Table S6 Performance of p–i–n OPVs prepared with THF SVA for 60 s after the deposition of either the i- or n-layer.$^{a,b}$

| Entry | Timing of SVA | $J_{SC}$ (mA cm$^{-2}$) | $V_{OC}$ (V) | FF (%) | PCE (%) | $R_{S}$ (Ω cm$^2$) | $R_{o}$ (Ω cm$^2$) |
|-------|---------------|--------------------------|-------------|--------|---------|-------------------|------------------|
| S17   | After i-layer deposition | 10.8 | 0.88 | 53.6 | 5.1 | 10 | 487 |
| S18   | After n-layer deposition | 9.34 | 0.87 | 55.0 | 4.5 | 10 | 596 |

$^{a}$Data of the best-performing devices. $^{b}$General device structure: [ITO/PEDOT:PSS (30 nm)/PhBADT (1 mg mL$^{-1}$ in CHCl$_3$)/AID:PC$_{71}$BM (1:1 by weight, 8 mg mL$^{-1}$ in CHCl$_3$)/ETL-1 (0.5 mg mL$^{-1}$ in MeOH)/Al (80 nm)]. The concentrations are of the cast solutions.

### Table S7 Performance of p–i–n OPVs prepared with THF SVA for different durations after the deposition of the i-layer.$^{a,b}$

| Entry | SVA duration | $J_{SC}$ (mA cm$^{-2}$) | $V_{OC}$ (V) | FF (%) | PCE (%) | $R_{S}$ (Ω cm$^2$) | $R_{o}$ (Ω cm$^2$) |
|-------|--------------|--------------------------|-------------|--------|---------|-------------------|------------------|
| S19   | 60           | 12.0 | 0.88 | 54.7 | 5.7 | 10 | 481 |
| S20   | 90           | 12.2 | 0.88 | 53.1 | 5.7 | 11 | 450 |
| S21   | 120          | 12.7 | 0.88 | 52.6 | 5.9 | 11 | 411 |
| S22   | 150          | 12.7 | 0.88 | 51.5 | 5.8 | 12 | 412 |
| S23   | 180          | 12.7 | 0.88 | 51.8 | 5.8 | 13 | 410 |

$^{a}$Data of the best-performing devices. $^{b}$General device structure: [ITO/PEDOT:PSS (30 nm)/PhBADT (1 mg mL$^{-1}$ in CHCl$_3$)/AID:PC$_{71}$BM (1:1 by weight, 8 mg mL$^{-1}$ in CHCl$_3$)/ETL-1 (0.5 mg mL$^{-1}$ in MeOH)/Al (80 nm)]. The concentrations are of the cast solutions.

### 3.2.4. Comparison of cathode buffers

Calcium and ETL-1 were compared as cathode buffer in p–i–n devices having a general structure of [ITO/PEDOT:PSS/DTA/PC$_{71}$BM/ PC$_{71}$BM/buffer/Al]. DTA was deposited by spin-coating of DTADK (5 mg mL$^{-1}$ in CHCl$_3$) at 800 rpm for 30 s, followed by irradiation with a blue LED (470 ± 10 nm) at 0.5 W cm$^{-2}$ for 10 min. The i-layer was prepared by spin-coating of AtDDK:PC$_{71}$BM (1:1 by weight, 8 mg mL$^{-1}$ in CHCl$_3$) followed by irradiation with the same LED at 1 W cm$^{-2}$ for 30 min. PC$_{71}$BM was spin-coated from a 5 mg mL$^{-1}$ solution in CHCl$_3$. Calcium (10 nm) was vapor-deposited at high vacuum (~$10^{-5}$ Pa) through a shadow mask, whereas ETL-1 was spin-coated from a 0.5 mg mL$^{-1}$ solution in methanol at 800 rpm for 30 s. Aluminum (80 nm) was vapor-deposited at high vacuum (~$10^{-5}$ Pa) through a shadow mask.
Table S8 Performance of p–i–n OPVs having calcium or ETL-1 as cathode buffer.\textsuperscript{a,b}

| Entry | Cathode buffer | J\textsubscript{SC} (mA cm\textsuperscript{-2}) | V\textsubscript{OC} (V) | FF (%) | PCE (%) | R\textsubscript{s} (\Omega \text{ cm}^2) | R\textsubscript{p} (\Omega \text{ cm}^2) |
|-------|----------------|------------------|-----------------|-------|--------|----------------|----------------|
| S24   | Ca             | 9.26              | 0.88            | 44.2  | 3.6    | 22             | 331            |
| S25   | ETL-1          | 9.92              | 0.89            | 47.5  | 4.2    | 17             | 369            |

\textsuperscript{a}Data are of the best-performing devices. \textsuperscript{b}General device structure: [ITO/PEDOT:PSS (30 nm)/DTA (5 mg mL\textsuperscript{-1} in CHCl\textsubscript{3})/AtD:PC\textsubscript{71}BM (1:1 wt. 8 mg mL\textsuperscript{-1})/Ca (10 nm) or ETL-1 (0.5 mg mL\textsuperscript{-1} in MeOH)/Al (80 nm)]. The concentrations are of the cast solutions.

3.3. Estimation of the material composition in the optimized p–i–n-type active layer

The amount of each component in the p–i–n active layer was estimated through fitting analysis of photoabsorption spectra. Fig. S6a shows photoabsorption spectra of PhBADT, AtD, and PC\textsubscript{71}BM in the thin film state, while Fig. S6b compares an absorption spectrum of a p–i–n-type active layer with a simulated one. The simulated spectrum was obtained as a weighted sum of the three spectra in Fig. S6a, and the ratio of the three components was estimated as 1:3:10 on the basis of the absorbance per thickness. The total thickness of the p–i–n-type active layer was measured to be about 80 nm, and thus the thicknesses of sublayers could be calculated as ca. 5, 33, 41 nm for the p, i, n-layers, respectively. Note that the interlayer mixing was not taken into account in this estimation.

Fig. S6 (a) Photoabsorption spectra of thin films of PhBADT, AtD and PC\textsubscript{71}BM. Absorbance is normalized per film thickness. Thin films were prepared on glass plates by spin-coating a chloroform solution of PhBADT\textsubscript{DK} (1 mg mL\textsuperscript{-1}), AtDDK (3.5 mg mL\textsuperscript{-1}), or PC\textsubscript{71}BM (7 mg mL\textsuperscript{-1}) at 800 rpm for 30 s. The photoconversion to PhBADT and AtD was performed by irradiating with a blue LED (\(\lambda = 470 \pm 10\) nm) at 0.5 W cm\textsuperscript{-2} for 10 min and 1 W cm\textsuperscript{-2} for 30 min, respectively. (b) Comparison of an experimental photoabsorption spectrum of a p–i–n-type active layer with a simulated spectrum. The simulated spectrum was obtained as a weighted sum of the three spectra shown in (a) (PhBADT:AtD:PC\textsubscript{71}BM \(\approx 1:3:10\)). The p–i–n film was prepared according to the procedure for the optimized device.
3.4. Stability of PC$_{71}$BM under the irradiation in the photoprecursor approach

Essentially no difference was observed between photoabsorption spectra before and after the irradiation with a blue LED at 1 W cm$^{-2}$ for 30 min (Fig. S7a). Additionally, the irradiated film dissolved completely upon rinse with chloroform (Fig. S7b). These data indicate that the [2 + 2] dimerization or oligomerization of PC$_{71}$BM would not be significant, if any, during the irradiation in the photoprecursor approach.

![Fig. S7](a) Photoabsorption spectra of PC$_{71}$BM thin films with or without irradiation with a blue LED. Irradiation conditions: 470 ± 10 nm, 1 W cm$^{-2}$, 30 min. The spectra were normalized at 379 nm. (b) Change in photoabsorption of a PC$_{71}$BM thin film before and after rinse with chloroform. The sample film was exposed to 470-nm light as described in (a) in advance.

4. Chemical synthesis

4.1. General

All reactions were carried out under argon unless otherwise noted. “Room temperature” (rt) means 25 ± 5 °C. $^1$H and $^{13}$C{$^1$H} nuclear magnetic resonance (NMR) spectra were acquired on a JEOL JNM-ECX400 (400 MHz) or JNM-ECA600 (600 MHz) spectrometer at 298 K with the tetramethylsilane resonance as internal standards (0 ppm) whenever possible or solvent resonances otherwise ($^1$H: 5.32 ppm for CH$_2$Cl$_2$, $^{13}$C{$^1$H}: 53.84 ppm for CD$_2$Cl$_2$). Infrared (IR) spectra were recorded on a Jasco FT/IR-4200 spectrometer with the transmission configuration using KBr pellets, with an ATR PRO450-S attachment, or with an RAS PRO410-H attachment. Mass spectra were acquired on a JEOL Msation/JMS-700, JEOL AccuTOF/JMS-T100LC, or JEOL SpiralTOF/JMS-S3000 instrument. Material purification by flash column chromatography was performed on silica gel purchased from Kanto Chemical (Silica Gel 60N, 60 Å, 40–50 μm). Analytical thin-layer chromatography (TLC) was performed on Merck 200-μm thickness silica gel 60 plates with a fluorescent
indicator. Visualization was accomplished with UV light at 254 nm. Gel permeation chromatography was performed on a JAI recycling preparative HPLC LC-9204 system equipped with a JAI UV detector 310B (detected at 254 nm) and JAIGEL-2.5H-40 and -2H-40 columns using CHCl₃ as eluent.

4.2. Materials

Dehydrated-grade reaction solvents (THF, o-xylene, toluene, CH₂Cl₂, and (CH₃)₂SO) were purchased from Kanto Chemical or Wako Pure Chemical Industries and used as received. Non-dehydrated reaction solvents (xylenes and ethanol) were purchased from Wako Pure Chemical Industries or Nacalai Tesque. (i-Pr)₂NEt was distilled and stored over KOH under argon atmosphere. The cathode buffer material ETL-1 was prepared according to literature. Other reagents were obtained from commercial sources and used without further purification.

4.3. Synthesis of PhBADTDK

The synthesis of PhBADTDK is outlined in Scheme S1. The bent-anthradithiophene (BADT) framework was constructed by indium(III)-catalyzed cyclization of a diethynylbenzene derivative developed by Mamane et al. This method gave us a higher yield than the iodine-assisted photocyclization of the corresponding divinylbenzene derivative reported by Pietrangelo et al., which was used in the original synthesis of PhBADT. The target compound was obtained via three steps from PhBADT in an overall yield of 17%.

Scheme S1 Synthesis of PhBADTDK.
**Compound S2.** To a solution of 2-phenylthiophene (1.31 g, 8.21 mmol) in THF (50 mL) was added 1.55 M n-butyllithium in hexanes (7.0 mL, 11 mmol) at –78 °C over a period of 10 min, and the mixture was stirred at the same temperature for 1 h. A solution of ZnCl$_2$ (1.75 g, 12.8 mmol) in THF (30 mL) was added dropwise through a cannula over a period of 20 min. After the mixture was stirred for 1 h at rt, compound S1 (0.80 g, 1.9 mmol) and Pd(PPh$_3$)$_4$ (0.12 g, 0.10 mmol) were added against a counter-flow of argon. After refluxing for 16 h, the mixture was filtered through a pad of Celite, concentrated under reduced pressure to a volume of around 20 mL, and poured to 100 mL of saturated NH$_4$Cl aq. The mixture was extracted with CHCl$_3$ (2 × 100 mL). The combined organic layer was washed with brine (200 mL), dried over Na$_2$SO$_4$, filtered, and evaporated under vacuum. The resulting crude product was purified by flash silica gel column chromatography (hexanes/CHCl$_3$, 3:1) to give S2 as a white solid (0.67 g, 1.1 mmol, 60%). $^1$H NMR (400 MHz, CDCl$_3$): δ 0.29 (s, 18H), 7.30–7.33 (m, 4H), 7.41 (t, $J = 7.4$ Hz, 4H), 7.66 (d, $J = 7.1$ Hz, 4H), 7.73 (d, $J = 3.8$ Hz, 2H), 7.80 (s, 2H); $^{13}$C{$_1^1$H} NMR (100 MHz, CDCl$_3$): –0.36, 101.9, 104.2, 120.2, 123.3, 125.7, 127.7, 128.3, 128.9, 134.0, 134.1, 134.2, 139.8, 144.9; IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) 2957, 2924, 2158, 1485, 1459, 1285, 1459, 1250, 859, 756; HRMS (EI): m/z calcd for C$_{36}$H$_{34}$S$_2$Si$_2$+ (M$^+$) 586.1641, found 586.1640.

**PhBADT.** To a solution of compound S2 (4.18 g, 7.12 mmol) in THF (140 mL) was added dropwise a 1.0 M solution of (n-Bu)$_4$NF in THF (25 mL, 25 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 3.5 h before being concentrated under vacuum to a volume of around 50 mL. The resulting mixture was cooled down to 0 °C, and the solid was isolated by filtration then partitioned between chloroform (200 mL) and saturated NH$_4$Cl aq (200 mL). The organic layer was collected, and the aqueous layer was extracted with CHCl$_3$ (2 × 100 mL). The combined organic layers were washed with brine (200 mL), dried over Na$_2$SO$_4$, filtered, and evaporated under vacuum. The resulting solid was recrystallized from CHCl$_3$ and further purified by silica gel column chromatography (hexanes/CHCl$_3$, 4:1; then CHCl$_3$) to give the desilylated compound as a yellow solid (2.90 g, 6.55 mmol, 92%). Complete removal of the trimethylsilyl groups was confirmed by $^1$H NMR (CDCl$_3$, 400 MHz): δ 3.44 (s, 2H), 7.29–7.33 (m, 4H), 7.41 (t, $J = 7.5$ Hz, 4H), 7.66 (d, $J = 7.0$ Hz, 4H), 7.70 (d, $J = 4.0$ Hz, 2H), 7.83 (s, 2H).
The desilylated compound (0.522 g, 1.18 mmol), InCl₃ (67 mg, 0.30 mmol), and o-xylene (45 mL) were added to a Schlenk flask. The resultant mixture was stirred at 120 °C for 20 hours. After removal of the solvent under vacuum, the crude product was purified by recrystallization from chloroform at 0 °C to give the target compound as a pale yellow solid (0.317 g, 0.716 mmol, 61%). ¹H NMR (CDCl₃, 400 MHz): δ 7.37 (t, J = 7.6 Hz, 2H), 7.48 (t, J = 7.5 Hz, 4H), 7.70 (s, 2H), 7.80–7.82 (m, 6H), 7.91 (d, J = 8.8 Hz, 2H), 8.69 (s, 2H); IR (ATR): ʋ (cm⁻¹) 3057, 1597, 1512, 1481, 1442, 1271, 1172, 1072, 986, 935, 880, 837, 802, 758, 746; HRMS (EI): m/z calcd for C₃₀H₁₈S₂⁺ (M⁺) 442.0844, found 442.0848. Clear ¹³C NMR data could not be obtained because of the low solubility.

**Compound S3.** PhBADT (0.35 g, 0.79 mmol) and vinylene carbonate (11 mL, 15 g, 0.17 mol) in xylenes (90 mL) were heated in an autoclave at 180 °C for 3 days. Note that the reaction was performed without caring air and moisture. The reaction mixture was cooled to rt and the solvent was evaporated under vacuum. CH₂Cl₂ was added to the resulting mixture, and the insoluble black material was removed by filtration. The filtrate was purified by flash silica gel column chromatography (hexanes/CHCl₃, 1:1; then CHCl₃) to give S3 as a pale yellow solid (0.18 g, 0.34 mmol, 43%). ¹H NMR (CDCl₃, 400 MHz): δ 5.01–5.07 (m, 2H), 5.10 (d, J = 3.3 Hz, 1H), 5.14 (d, J = 3.4 Hz, 1H), 7.34–7.40 (m, 2H), 7.42–7.49 (m, 6H), 7.54 and 7.56 (two s, 2H), 7.62 and 7.65 (two d, J = 7.9 Hz, 2H), 7.71–7.74 (m, 4H); ¹³C{¹H} NMR (CDCl₃, 100 MHz): 46.3, 46.4, 46.5, 46.5, 76.0, 76.4, 120.0, 120.1, 120.2, 122.5, 122.6, 122.6, 123.5, 126.5, 128.4, 128.7, 128.9, 129.0, 131.0, 131.5, 132.0, 132.9, 133.7, 134.0, 136.3, 137.4, 140.8, 140.9, 144.2, 144.6, 153.9; IR (ATR): ʋ (cm⁻¹) 1805, 1488, 1449, 1403, 1361, 1152, 1076, 1052, 847, 760, 746; HRMS (EI): m/z calcd for C₃₃H₂₂O₂S₂⁺ (M⁺) 528.0843, found 528.0835.

**Compound S4.** To a solution of compound S3 (338 mg, 0.639 mmol) in THF (100 mL) was added dropwise a solution of 1.0 M NaOH (100 mL, 100 mmol) in air, and the mixture was stirred at rt for 14 h. The mixture was acidified with 6 M HCl (20 mL) and extracted with AcOEt (3 × 100 mL). The combined organic layer was washed with brine (500 mL), dried over Na₂SO₄, filtered, and evaporated under vacuum. The crude product was purified by flash silica gel column chromatography (CHCl₃) to give diol S4 as a pale yellow solid (220 mg, 0.437 mmol, 68%). ¹H NMR (CDCl₃, 400 MHz): δ 1.26 and 1.27 (two overlapping s, 2H), 4.13–4.20 (m, 2H), 4.82 (d, J = 2.9 Hz, 1H), 4.86 (d, J = 2.9 Hz, 1H), 7.33–7.48 (m, 8H), 7.50 (d, J = 7.3 Hz, 2H), 7.55
(d, J = 7.7 Hz, 1H), 7.59 (d, J = 7.7 Hz, 1H), 7.71–7.73 (m, 4H), 13C {1H} NMR (CDCl₃, 100 MHz): δ 49.9, 50.2, 67.8, 68.6, 120.0, 121.4, 121.6, 122.0, 123.7, 126.4, 128.2, 128.3, 128.9, 129.0, 133.4, 133.8, 134.1, 134.2, 135.1, 135.8, 137.8, 140.1, 140.1, 143.5, 143.7; IR (ATR): ν (cm⁻¹) 3378, 3055, 2942, 1488, 1449, 1401, 1167, 1070, 1004, 845, 760, 748; HRMS (ESI): m/z calcd for C₃₂H₂₂O₂S₂Na⁺ ([M + Na⁺]⁺) 525.0953, found 525.0952.

PhBADTDK. (CF₃CO)₂O (2.2 ml, 3.3 g, 16 mmol) was added dropwise to a stirred solution of (CH₃)₂SO (2.2 mL, 2.4 g, 31 mmol) in CH₂Cl₂ (4 mL) at −60 °C. After stirring at the same temperature for 15 min, a solution of compound S₄ (310 mg, 0.618 mmol) in CH₂Cl₂ (10 mL) was added to the reaction. The mixture was further stirred at −60 °C for 1.5 h, and then (i-Pr)₂NEt (5.9 mL, 4.4 g, 34 mmol) was added dropwise. After stirring for 1 h at the same temperature, the reaction was allowed to warm up to rt and further stirred for 40 min. The mixture was quenched with 1 M HCl (20 mL) and extracted with CH₂Cl₂ (3 × 20 mL). The combined organic layer was washed with H₂O (3 × 20 mL) and brine (40 mL), dried over Na₂SO₄, filtered, and evaporated under vacuum. The crude product was purified by flash silica gel column chromatography (CH₂Cl₂). The isolated material was further purified by recrystallization from toluene and CHCl₃ to give the pure target compound as an orange solid (175 mg, 0.351 mmol, 57%). ¹H NMR (CDCl₃, 400 MHz): δ 5.36 (s, 2H), 7.38 (t, J = 7.3 Hz, 2H), 7.46 (t, J = 7.3 Hz, 4H), 7.52 (d, J = 8.1 Hz, 2H), 7.59 (s, 2H), 7.72 (d, J = 7.3 Hz, 4 H), 7.78 (d, J = 7.9 Hz, 2H), 13C {1H} NMR (CDCl₃, 151 MHz): δ 58.1, 120.1, 123.0, 124.6, 126.6, 128.9, 129.1, 130.2, 133.6, 136.9, 142.2, 145.5, 181.7; IR (ATR): ν (cm⁻¹) 1750, 1731, 1487, 1447, 1405, 1107, 851, 761, 733; HRMS (ESI): m/z calcd for C₃₂H₁₈O₂S₂Na⁺ ([M + Na⁺]⁺) 521.0640, found 521.0646.

4.4. Synthesis of AtDDK

Scheme S2 outlines the synthesis of AtDDK. The synthesis was started with the condensation cyclization between naphthalene-1,4-diol (S₅) and 5-bromo-2,3-thiophenedicarboxaldehyde (S₆) under basic conditions. The resulting quinone S₇ was reduced to the corresponding bromoanthrathiophene S₈. The Diels–Alder reaction of S₈ and vinylene carbonate afforded adduct S₉, which was coupled with stannylated diketopyrrolopyrrole S₁₁ to form S₁₂. The carbonate moieties were converted to α-diketone via hydrolysis followed by Swern oxidation to afford the target photoprecursor AtDDK.
**Scheme S2 Synthesis of AtDDK.**

**Compound S7.** Compounds S5 (1.71 g, 10.7 mmol) and S6 (2.24 g, 10.2 mmol) were dissolved in ethanol (120 mL), to which 1 M KOH aq. (30 mL, 30 mmol) was added dropwise. The mixture was stirred at rt for 1 h in air. The resulting brown precipitate was collected by filtration and washed sequentially with water and methanol to afford compound S7 as a brown solid (3.02 g, 8.80 mmol, 88%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.59, (s, 1H), 7.83 (m, 2H), 8.36 (m, 2H), 8.64 (s, 1H), 8.71 (s, 1H); IR (KBr): $\tilde{\nu}$ (cm$^{-1}$) 3309, 3089, 1665, 1632, 1611, 1577, 1514, 1495, 1475, 1447, 1406, 1373, 1332, 1307, 1288, 1264, 1233, 1167, 961, 943, 928, 837, 788; HRMS (ESI): $m/z$ calcld for C$_{16}$H$_7$BrO$_2$S$^+$ (M$^+$) 341.9345, found 341.9354. $^{13}$C $^1$H NMR was not obtained because of the low solubility.

**Compound S8.** Quinone S7 (3.00 g, 8.74 mmol) was suspended in THF (60 mL) and ethanol (30 mL) in air. NaBH$_4$ (1.98 g, 52.3 mmol) was added to the suspension at 0 °C and stirred at the same temperature for 1 h before 6 M HCl (80 mL) was added dropwise at 0 °C. The mixture was warmed up and stirred at reflux for 1
h. After cooling down to rt, water (50 mL) was added to the reaction. The yellow precipitate was collected by filtration and washed sequentially with water and methanol, and then dried in vacuo. The solid was suspended in THF (60 mL) and ethanol (30 mL) in air. NaBH₄ (6.74 g, 178 mmol) was added to the suspension at 0 °C, and the resultant mixture was stirred at 60 °C for 21 h before 6 M HCl (80 mL) was added dropwise at 0 °C. The mixture was further stirred at 60 °C for 15 min then cooled down to rt. Water (50 mL) was added to the reaction. The yellow precipitate was collected by filtration and washed sequentially with water, methanol, and AcOEt. The solid was dried in vacuo to provide the target compound S8 as a yellow powder (1.86 g, 5.94 mmol, 68%). ¹H NMR (400 MHz, CDCl₃): δ 7.42 (s, 1H), 7.44 (m, 2H), 8.01 (m, 2H), 8.36 (s, 1H), 8.38 (s, 1H), 8.48 (s, 1H), 8.57 (s, 1H); IR (KBr): ν (cm⁻¹) 3077, 3051, 1515, 1407, 1284, 1268, 1237, 1128, 1026, 956, 935, 898, 856, 818, 739, 716; HRMS (ESI): m/z calcd for C₁₉H₉BrS⁺ ([M⁺]⁺) 311.9603, found 311.9605.

Compound S9. A solution of compound S8 (0.73 g, 2.3 mmol) and vinylene carbonate (2.0 mL, 2.7 g, 31 mmol) in xylene (50 mL) was heated in an autoclave at 150 °C for 17 h. Note that the reaction was performed without caring air and moisture. After cooled down to rt, the reaction mixture was transferred to a round-bottom flask with CHCl₃ and evaporated in vacuo. The crude was subjected to chromatography on silica gel (CH₂Cl₂/hexanes, 3:1). The resulting material was dissolved in a small amount of CHCl₃ and poured to diethyl ether. The precipitate was collected by filtration and washed with diethyl ether to provide the target compound as a grayish powder (700 mg, 1.75 mmol, 76%). ¹H NMR (400 MHz, CDCl₃): δ 4.76 (m, 2H), 4.93 (m, 2H), 7.24–7.29 (m, partially overlapping with CHCl₃), 7.39 (m, 2H), 7.70 (s, 1H), 7.74 and 7.75 (two s, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 47.7, 47.7, 47.6, 76.1, 76.2, 76.3, 115.7, 116.1, 118.7, 119.7, 120.7, 125.7, 126.2, 126.3, 126.7, 127.9, 128.0, 132.8, 133.2, 134.1, 134.5, 135.9, 136.1, 137.4, 137.7, 138.7, 138.8, 140.1, 140.2, 154.0; IR (KBr): ν (cm⁻¹) 1853, 1802, 1454, 1415, 1367, 1174, 1161, 1054, 940, 762; HRMS (ESI): m/z calcd for C₁₉H₁₁BrNaO₃S⁺ ([M + Na⁺]⁺) 420.9504, found 420.9512.

Compound S11. To a solution of diisopropylamine (1.40 mL, 1.00g, 9.91 mmol) in THF (20 mL) was added 2.6 M n-butyllithium in hexanes (3.5 mL, 9.1 mmol). The resultant solution of lithium diisopropylamide was added to a THF solution (15 mL) of S10 (690 mg, 1.31 mmol) and tributyltin chloride (2.20 mL, 2.64 g, 8.11 mmol) at −25 °C over 1 h. The reaction was stirred at −25 °C for 30 min then at rt for 25 h. After the solvent
was removed under vacuum, the mixture was purified by column chromatography on silica gel containing 10\% K$_2$CO$_3$ (hexanes/CH$_2$Cl$_2$, 2:1) to give S11 as a dark red solid (1.23 g, 1.11 mmol, 74\%). $^1$H NMR (400 MHz, CDCl$_3$): δ 0.84–0.94 (m, 30H), 1.04–1.40 (m, 38H), 1.48–1.68 (m, 14H), 1.85–1.93 (m, 2H), 4.02–4.13 (m, 4H), 7.28–7.34 (m, 2H), 9.10 (d, J = 3.7 Hz, 2H); $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$): δ 10.5, 11.1, 13.7, 14.1, 23.2, 23.6, 27.2, 28.5, 29.0, 30.3, 39.2, 45.9, 107.0, 135.3, 136.3, 136.5, 139.8, 145.4, 161.9.

**Compound S12.** Compound S9 (545 mg, 1.37 mmol), compound S11 (711 mg, 0.645 mmol), Pd(PPh$_3$)$_4$ (78.2 mg, 0.0676 mmol) were dissolved in toluene (100 mL) in a round-bottom flask. The reaction mixture was refluxed for 6 h before concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (CH$_2$Cl$_2$/EtOAc, 40:1) and gel permeation chromatography (CHCl$_3$) to yield the target compound as a deep blue solid (0.547 g, 0.471 mmol, 73\%). $^1$H NMR (400 MHz, CD$_2$Cl$_2$): δ 0.86–0.92 (m, 12H), 1.27–1.42 (m, 16H), 1.90 (broad s, 2H), 3.97–4.08 (m, 4H), 4.80 (broad s, 4H), 4.96–4.97 (m, 4H), 7.26–7.32 (m, 4H), 7.39–7.46 (m, 6H), 7.53 (broad s, 2H), 7.78–7.84 (m, 4H), 8.90–8.93 (m, 2H); $^{13}$C($^1$H) NMR (100 MHz, CD$_2$Cl$_2$): δ 10.7, 14.3, 23.5, 24.0, 28.9, 30.7, 39.7, 46.2, 48.1, 48.2, 76.6, 76.7, 76.7, 109.2, 119.8, 120.6, 121.1, 121.3, 122.0, 126.1, 126.5, 127.0, 128.1, 128.3, 130.0, 134.4, 135.4, 135.4, 136.6, 136.8, 137.0, 137.2, 137.9, 138.2, 139.3, 139.6, 139.8, 139.9, 142.4, 154.3, 154.4, 161.8; IR (KBr): $\tilde{\nu}$ (cm$^{-1}$) 3073, 3048, 3025, 2956, 2928, 2870, 2858, 2360, 1842, 1808, 1663, 1557, 1527, 1460, 1438, 1416, 1401, 1361, 1225, 1150, 1078, 1053, 883, 811, 760, 734; HRMS (MALDI–TOF): m/z calcd for C$_{68}$H$_{60}$N$_2$O$_8$S$_4$+ (M$^+$) 1160.3227, found 1160.3231.

**Compound S13.** In a 300 mL round-bottom flask, compound S12 (505 mg, 0.434 mmol) was dissolved in THF (120 mL) in air. After the addition of 1.5 M NaOH aq (30 mL), the mixture was stirred vigorously at rt for 10 h. The mixture was poured into water (100 mL) and extracted with AcOEt (3 × 100 mL). The combined organic layer was washed with water (100 mL) then brine (100 mL), dried over Na$_2$SO$_4$, filtered, and evaporated under vacuum. The resulting solid was recrystallized from CH$_2$Cl$_2$ by adding hexanes to yield the hydrolyzed compound S13 as a blue solid (428 mg, 0.386 mmol, 89\%). The complete hydrolysis was confirmed by $^1$H NMR and the material was used without further purification in the next step because of the low solubility. $^1$H NMR (400 MHz, CD$_3$SO): δ 0.74 and 0.79 (two broad s, 12H), 1.14 and 1.22 (two broad s, 16H), 1.74 (broad s, 2H), 3.86 (broad s, 4H), 3.94 and 3.97 (two broad s, 4H), 4.46 (s, 4H), 4.72–4.78 (m, 4H), 7.13–7.16 (m, 4H), 7.32 (m, 2H), 7.38 (m, 2H), 7.69 and 7.70 (two overlapping s, 2H), 7.77–7.82 (m, 4H), 7.89 (s, 1H), 7.95–7.96.
(m, 1H), 8.83 (m, 2H); IR (KBr): \( \tilde{\nu} \) (cm\(^{-1}\)) 3443, 3378, 3069, 3042, 3025, 2955, 2927, 2871, 2857, 1640, 1553, 1522, 1455, 1435, 1401, 1225, 1156, 1102, 1075, 1021, 1004, 878, 812, 751, 733, 711; HRMS (MALDI–TOF) \( m/z \) calcd for C\(_{66}\)H\(_{64}\)N\(_2\)O\(_6\)S\(_4\) (M\(^+\)) 1108.3642, found 1108.3612. \(^{13}\)C\{\(^{1}\)H\} NMR was not obtained because of the low solubility.

**AtDDK.** (CF\(_3\))\(_2\)O (0.46 mL, 0.69 g, 3.3 mmol) was added dropwise to a round-bottom flask containing CH\(_2\)Cl\(_2\) (7.0 mL) and (CH\(_3\))\(_2\)SO (2.0 mL) at –65 °C. After stirring for 1 h, to the mixture was added dropwise compound S\(_{13}\) (80.6 mg, 0.0726 mmol) dissolved in (CH\(_3\))\(_2\)SO (6 mL) and CH\(_2\)Cl\(_2\) (23 mL). Stirring was continued for 2 h at the same temperature. (i-Pr)\(_2\)NEt (1.2 mL, 0.89 g, 6.9 mmol) was added dropwise to the mixture, and the reaction was further stirred at –65 °C for 2 h before warmed up to rt and stirred for additional 30 min. The mixture was poured to water (50 mL), to which 3 M HCl (25 mL) was added before extraction with CH\(_2\)Cl\(_2\) (3 × 100 mL). The combined organic layer was washed with brine (100 mL), dried over Na\(_2\)SO\(_4\), filtered, and evaporated in vacuo. The crude product was recrystallized from CH\(_2\)Cl\(_2\) by adding CH\(_3\)CN, and further purified by flash column chromatography on silica gel (CH\(_2\)Cl\(_2\)/AcOEt, 30:1). The solid was dried in vacuo at 180 °C for 3 h to give AtDDK as a blue-black solid (50.1 mg, 0.0455 mmol, 63%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 0.86–0.94 (m, 12H), 1.24–1.43 (m, 16H), 1.92 (quint, 2H), 4.00–4.12 (m, 4H), 5.10 (s, 2H), 7.38–7.43 (m, 6H), 7.49–7.53 (m, 6H), 7.84 (s, 2H), 7.90 (s, 2H), 8.92 (d, \( J = 4.0 \) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 10.6, 14.1, 23.1, 23.7, 28.6, 30.4, 39.3, 46.0, 60.0, 60.1, 108.9, 120.0, 120.6, 121.2, 126.4, 126.6, 129.6, 129.7, 131.8, 132.0, 134.7, 134.9, 136.5, 137.7, 139.4, 140.5, 140.9, 141.7, 161.5, 183.8, 184.0; IR (KBr): \( \tilde{\nu} \) (cm\(^{-1}\)) 3069, 2958, 2927, 2872, 2856, 1739, 1665, 1557, 1506, 1457, 1431, 1403, 1381, 1338, 1226, 1163, 1099, 1073, 1022, 950, 879, 812, 798, 732, 709; HRMS (ESI): \( m/z \) calcd for C\(_{66}\)H\(_{64}\)N\(_2\)O\(_6\)S\(_4\)Na\(^+\) ([M + Na\(^+\)]) 1123.2913; found 1123.2927.
5. NMR spectra

$^1$H NMR spectrum of compound S2 (400 MHz, CDCl$_3$).

$^{13}$C $^1$H NMR spectrum of compound S2 (100 MHz, CDCl$_3$).
$^1$H NMR spectrum of PhBADT (400 MHz, CDCl$_3$).

$^1$H NMR spectrum of compound S3 (400 MHz, CDCl$_3$).
$^{13}$C{\textsuperscript{1}H} NMR spectrum of compound S3 (100 MHz, CDCl$_3$).

$^{1}$H NMR spectrum of compound S4 (400 MHz, CDCl$_3$).
13C{1H} NMR spectrum of compound S4 (100 MHz, CDCl₃).

1H NMR spectrum of PhBADTDK (400 MHz, CDCl₃).
$^{13}$C ($^1$H) NMR spectrum of PhBADTDK (151 MHz, CDCl$_3$).

$^1$H NMR spectrum of compound S7 (400 MHz, CDCl$_3$).
$^{1}$H NMR spectrum of compound S8 (400 MHz, CDCl$_3$).

$^{1}$H NMR spectrum of compound S9 (400 MHz, CDCl$_3$).
$^{13}$C\{\textsuperscript{1}H\} NMR spectrum of compound S9 (100 MHz, CDCl$_3$).

$^1$H NMR spectrum of compound S11 (400 MHz, CDCl$_3$).
$^{13}$C ($^1$H) NMR spectrum of compound S11 (100 MHz, CDCl$_3$).

$^1$H NMR spectrum of compound S12 (400 MHz, CD$_2$Cl$_2$).
$^{13}$C ($^1$H) NMR spectrum of compound S12 (100 MHz, CD$_2$Cl$_2$).

$^1$H NMR spectrum of compound S13 (400 MHz, DMSO-$d_6$).
$^1$H NMR spectrum of AtDDK (400 MHz, CDCl$_3$).

$^{13}$C\{\(^1\)H\} NMR spectrum of AtDDK (100 MHz, CDCl$_3$).
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