# *Supplementary Information*

## 2-Chloroalkoxy-Substituted Pentafluorinated Bistolanes as Novel Light-Emitting Liquid Crystals

Shigeyuki Yamada [1,*], Kazuya Miyano [1], Tomohiro Agou [2], Toshio Kubota [2] and Tsutomu Konno [1]

[1] Faculty of Molecular Chemistry and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan; Tel: +81-75-724-7517; E-mail: syamada@kit.ac.jp

[2] Department of Quantum Beam Science, Graduate School of Science and Engineering, Ibaraki University, 4-12-1 Naka-narusawa, Hitachi, Ibaraki 316-8511, Japan

* Correspondence: syamada@kit.ac.jp; Tel.: +81-75-724-7517

***Table of contents***

## 1. Crystal Structure

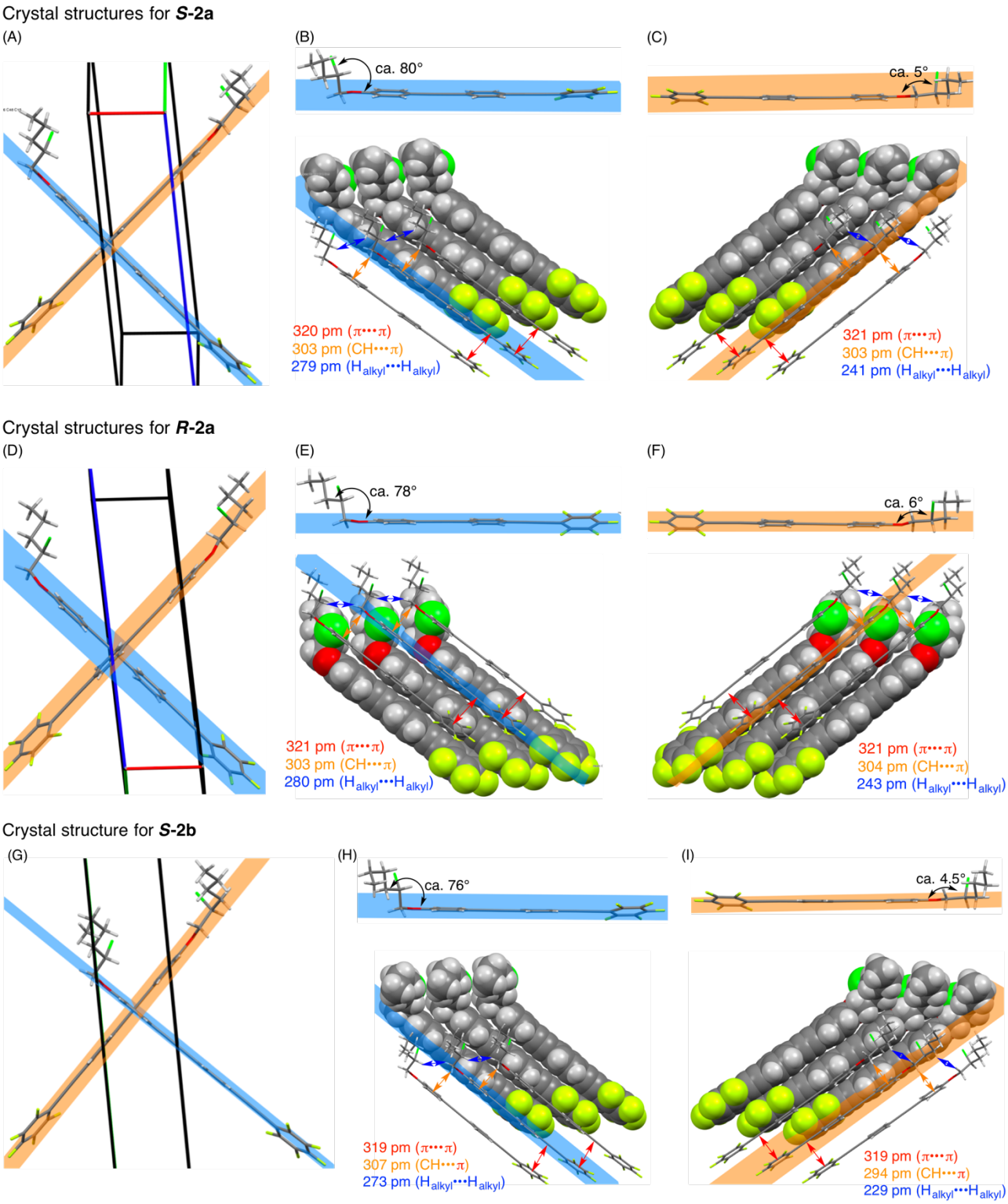



**Figure S1.** Crystal structures for ***S*-2a**, ***R*-2a** and ***S*-2b**. (A,D,G) Packing structures in a unit cell. (B,C) Packing structures of ***S*-2a** and intermolecular interactions observed. (E,F) Packing structures of ***R*-2a** and intermolecular interactions observed. (H,I) Packing structures of ***S*-2b** and intermolecular interactions observed.

**Table S1**. Crystallographic data for 2-chloroalkoxy-substituted bistolanes

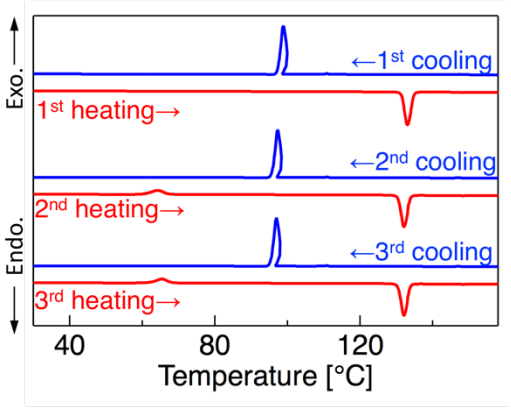
| | ***S*-2a** | ***R*-2a** | ***S*-2b** |
|---|---|---|---|
| CCDC No. | 1896325 | 1896324 | 1896326 |
| Empirical formula | $C_{27}H_{18}F_5ClO$ | $C_{27}H_{18}F_5ClO$ | $C_{28}H_{20}F_5ClO$ |
| Formula weight | 488.86 | 488.86 | 502.89 |
| Temperature [K] | 298(2) | 298(2) | 173(2) |
| Crystal color / Habit | Colorless / block | Colorless / Platelet | Colorless / Needle |
| Crystal size [mm] | 0.15 x 0.14 x 0.12 | 0.23 x 0.18 x 0.10 | 0.28 x 0.12 x 0.10 |
| Crystal system | Triclinic | Triclinic | Monoclinic |
| Space group | *P*1 | *P*1 | $P2_1$ |
| *a* [Å] | 4.9402(4) | 4.9482(2) | 4.9524(6) |
| *b* [Å] | 11.3656(8) | 11.3793(5) | 41.501(3) |
| *c* [Å] | 20.5539(13) | 20.6358(7) | 11.2392(10) |
| $\alpha$ [°] | 103.346(6) | 103.156(3) | 90 |
| $\beta$ [°] | 95.208(7) | 95.186(3) | 90.176(8) |
| $\gamma$ [°] | 90.248(7) | 90.283(3) | 90 |
| V [Å$^3$] | 1117.88(14) | 1126.45(8) | 2310.0(4) |
| Z | 2 | 2 | 4 |
| $R$ [$F^2>2\sigma(F^2)$] [a] | 0.0524 | 0.0388 | 0.0531 |
| $wR$ ($F^2$) [b] | 0.1204 | 0.0924 | 0.0943 |
| Flack parameter | –0.06(8) | 0.10(4) | 0.10(4) |

[a] $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. [b] $wR = \{[\Sigma w(|F_o| - |F_c|)]/\Sigma w|F_o|\}^{1/2}$.

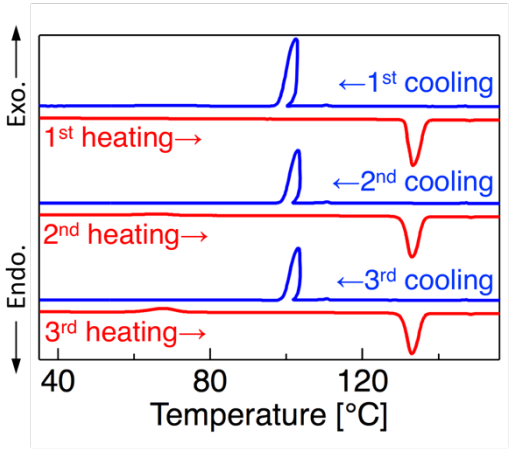
## 2. Differential Scanning Calorimetry (DSC)

Phase transition temperature of pentafluorinated tolane derivatives were determined with a differential scanning calorimeter (DSC, SII X-DSC7000 or SHIMADZU DSC-60-PLUS) at the rate of heating/cooling process of 5.0 °C $min^{-1}$.

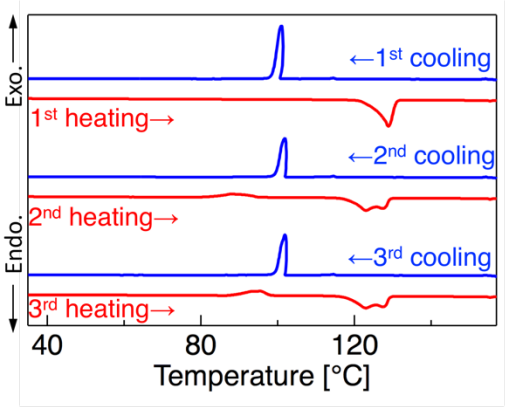
(A) **S-2b**



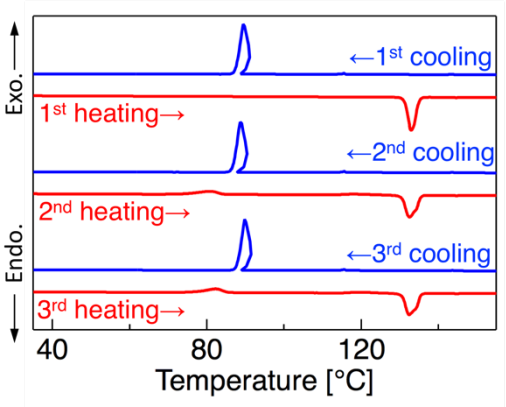

(B) **R-2a**




(C) **rac-2a**




(D) **S-2b**




(E) **rac-2b**

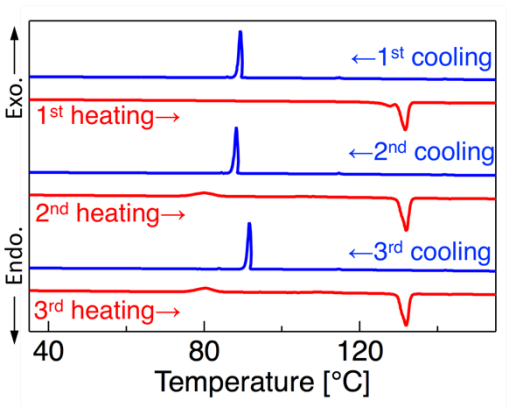
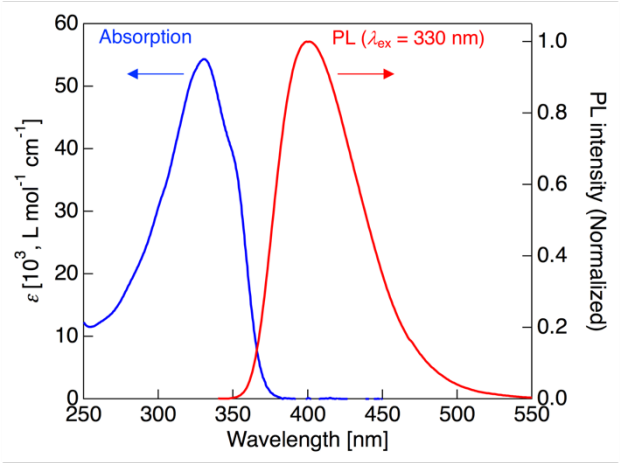



**Figure S2.** DSC thermograms of (A) ***S*-2a**, (B) ***R*-2a**, (C) ***rac*-2a**, (D) **S-2b** and (E) ***rac*-2b** under $N_2$ atmosphere.

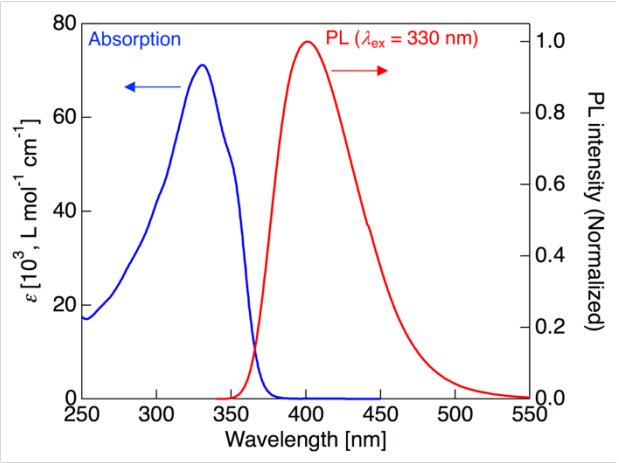
### 3. Absorption and PL Properties in Solution Phase

UV-vis absorption spectra were recorded using a JASCO V-500 absorption spectrometer. Steady-state PL spectra were obtained using a JASCO FP-8500 and a Hitachi F-7000 fluorometer.

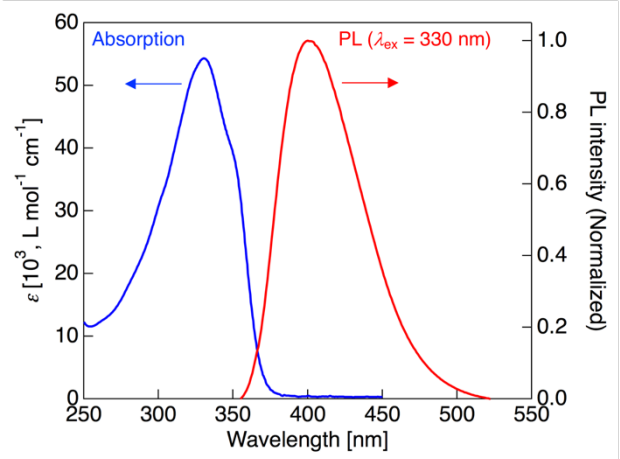
(A) ***S*-2a**



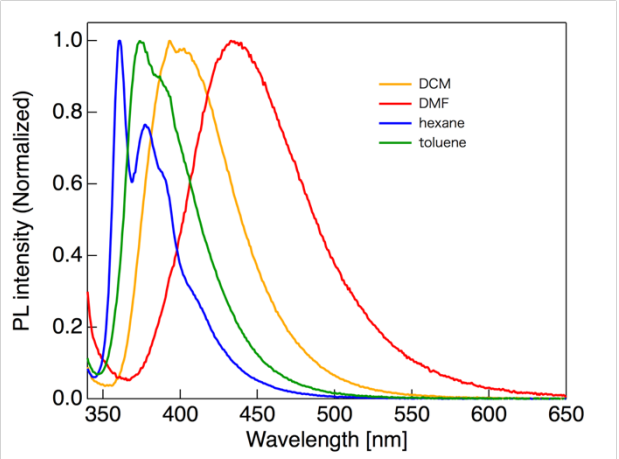

(B) ***R*-2a**



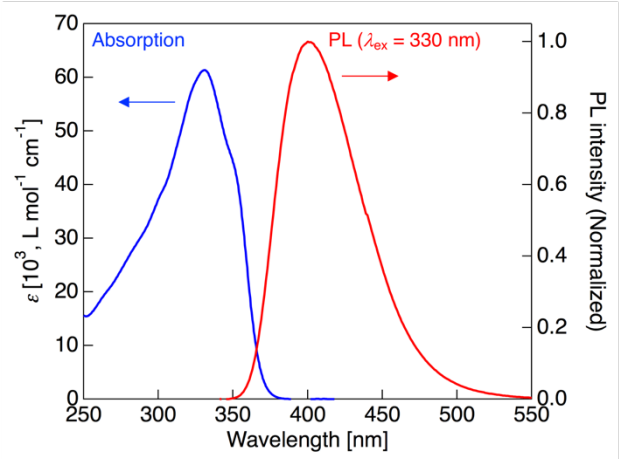

(C) ***rac*-2a**




(D) ***S*-2a** in various solvent




(E) ***S*-2b**




(F) ***rac*-2b**

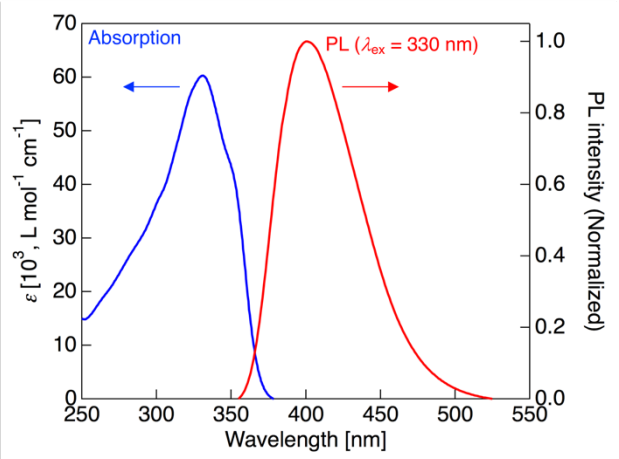
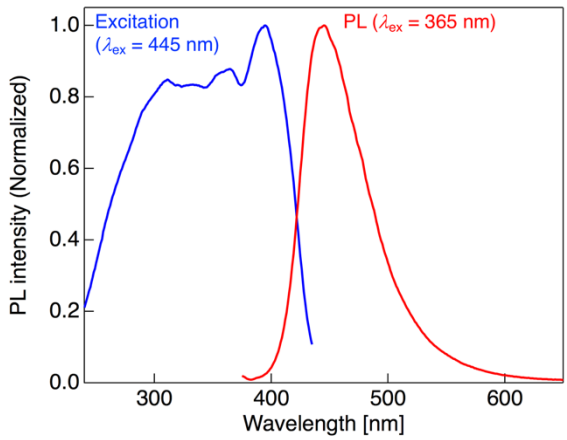



**Figure S3**. Absorption (blue line) and PL spectra (red line) for (A) ***S*-2a**, (B) ***R*-2a**, (C) ***rac*-2a**, (D) ***S*-2a** in various solvents, (E) ***S*-2b**, and (F) ***rac*-2b** measured in $CH_2Cl_2$ solution. Concentration: $1.0 \times 10^{-5}$ mol $L^{-1}$ for absorption and $1.0 \times 10^{-6}$ mol $L^{-1}$ for PL.

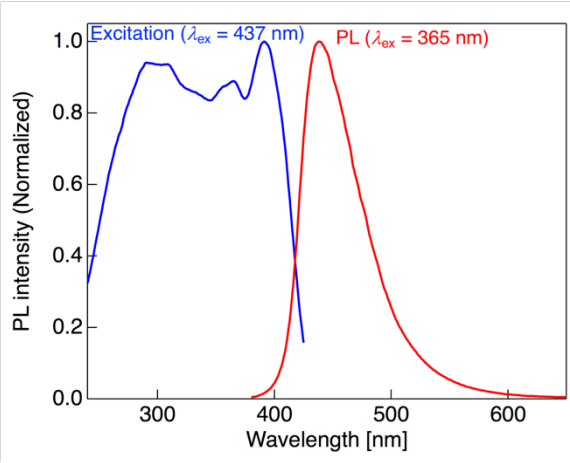
**4. Excitation and PL Properties in Cr Phase**

Steady-state PL spectra were obtained using a JASCO FP-8500 and a Hitachi F-7000 fluorometer.

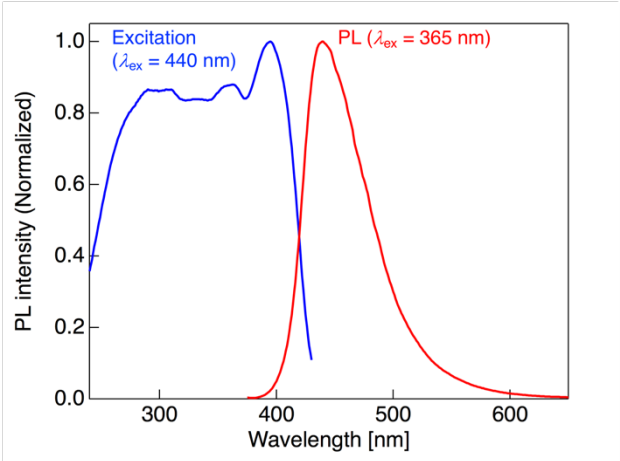
(A) ***S*-2a**



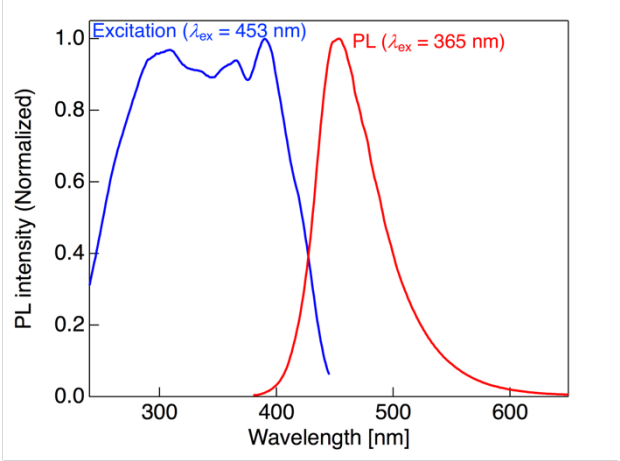

(B) ***R*-2a**




(C) ***rac*-2a**




(D) ***S*-2b**




(E) ***rac*-2b**

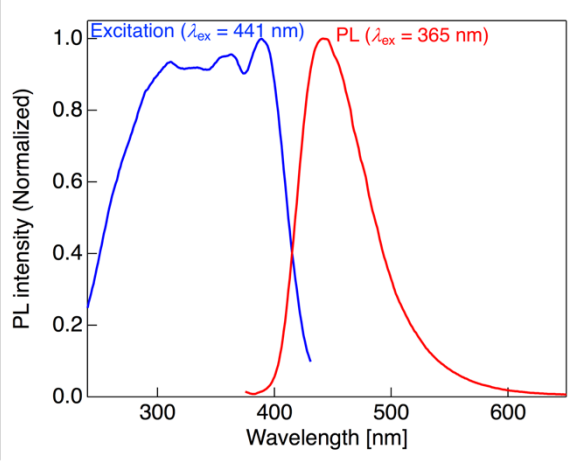



**Figure S4**. Excitation (blue line) and PL spectra (red line) for (A) ***S*-2a**, (B) ***R*-2a**, (C) ***rac*-2a**, (D) ***S*-2b**, and (E) ***rac*-2b** measured in Cr phase obtained after recrystallization.

## 5. Quantum chemical calculation

All computations were carried out using density functional theory (DFT) with the Gaussian 09 (Rev. C.01) package. Geometry optimizations were executed using the CAM-B3LYP hybrid functional and 6-31G(d) basis set with a CPCM model ($CH_2Cl_2$).

(A) HOMO (–7.13 eV) (B) LUMO (–1.28 eV)

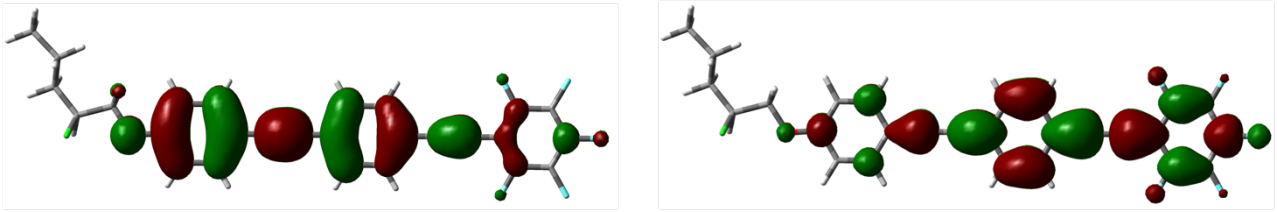


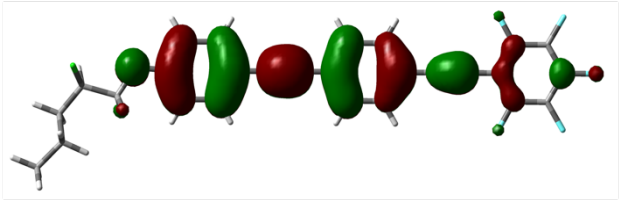
**Figure S5.** Molecular orbital diagrams for ***S*-2a** calculated by DFT//CAM-B3LYP/6-31+G(d) level of theory with a CPCM model.

SCF Done: E(RCAM-B3LYP) = –2073.53937254 A.U.
Dipole moment (Debye): X= –4.5846 Y= 2.9556 Z= –2.3223 Tot= 5.9285

**Table S2.** Cartesian Coordinate for ***S*-2a** at the ground state

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 17 | 0 | –10.352396 | –1.193612 | 1.220017 |
| 2 | 9 | 0 | 7.299003 | 2.497140 | 0.073601 |
| 3 | 9 | 0 | 9.988340 | 2.661604 | 0.141307 |
| 4 | 9 | 0 | 11.494278 | 0.398124 | 0.149966 |
| 5 | 9 | 0 | 7.601756 | –2.219026 | 0.021987 |
| 6 | 8 | 0 | –7.687167 | –0.959567 | –0.360212 |
| 7 | 9 | 0 | 10.290060 | –2.040510 | 0.089789 |
| 8 | 6 | 0 | –0.912056 | –0.404998 | –0.179591 |
| 9 | 6 | 0 | 2.685641 | –1.381767 | –0.114113 |
| 10 | 1 | 0 | 3.288597 | –2.283663 | –0.123625 |
| 11 | 6 | 0 | 0.512996 | –0.311616 | –0.140557 |
| 12 | 6 | 0 | –5.559777 | –1.925069 | –0.335122 |
| 13 | 1 | 0 | –6.054280 | –2.890173 | –0.373189 |
| 14 | 6 | 0 | 1.303941 | –1.471340 | –0.152329 |
| 15 | 1 | 0 | 0.825306 | –2.444087 | –0.191772 |
| 16 | 6 | 0 | –4.181126 | –1.833395 | –0.300439 |
| 17 | 1 | 0 | –3.580612 | –2.737226 | –0.311443 |
| 18 | 6 | 0 | –2.120261 | –0.484527 | –0.211941 |
| 19 | 6 | 0 | 2.526080 | 1.032148 | –0.051192 |
| 20 | 1 | 0 | 3.004962 | 2.004859 | –0.011693 |
| 21 | 6 | 0 | 10.164751 | 0.312362 | 0.116291 |
| 22 | 6 | 0 | 5.944382 | 0.042662 | 0.008165 |
| 23 | 6 | 0 | 4.738359 | –0.035720 | –0.024180 |
| 24 | 6 | 0 | 3.313872 | –0.128515 | –0.063092 |
| 25 | 6 | 0 | 9.548357 | –0.929277 | 0.085583 |
| 26 | 6 | 0 | –3.545778 | –0.579792 | –0.249540 |
| 27 | 6 | 0 | 9.394418 | 1.465258 | 0.112030 |
| 28 | 6 | 0 | –6.342570 | –0.765139 | –0.320289 |
| 29 | 6 | 0 | 7.361353 | 0.133318 | 0.045310 |
| 30 | 6 | 0 | 8.167783 | –1.008424 | 0.050837 |
| 31 | 6 | 0 | 8.015071 | 1.368387 | 0.077059 |
| 32 | 6 | 0 | –5.729642 | 0.487737 | –0.271965 |
| 33 | 1 | 0 | –6.312454 | 1.400430 | –0.262692 |
| 34 | 6 | 0 | –8.544811 | 0.170487 | –0.311095 |
| 35 | 1 | 0 | –8.377877 | 0.803597 | –1.192127 |
| 36 | 1 | 0 | –8.345516 | 0.757244 | 0.591100 |
| 37 | 6 | 0 | 1.144442 | 0.941114 | –0.089347 |
| 38 | 1 | 0 | 0.541799 | 1.843130 | –0.079680 |
| 39 | 6 | 0 | –4.341339 | 0.570720 | –0.236532 |
| 40 | 1 | 0 | –3.868697 | 1.546869 | –0.198481 |
| 41 | 6 | 0 | –9.976759 | –0.321116 | –0.339842 |
| 42 | 1 | 0 | –10.069532 | –1.090976 | –1.107141 |
| 43 | 6 | 0 | –10.994933 | 0.785375 | –0.594751 |
| 44 | 1 | 0 | –10.825647 | 1.137827 | –1.621240 |
| 45 | 1 | 0 | –11.993749 | 0.335621 | –0.584974 |
| 46 | 6 | 0 | –10.955665 | 1.974771 | 0.365202 |
| 47 | 1 | 0 | –9.985537 | 2.481530 | 0.296374 |
| 48 | 1 | 0 | –11.050827 | 1.616861 | 1.396592 |
| 49 | 6 | 0 | –12.067276 | 2.979064 | 0.067770 |
| 50 | 1 | 0 | –11.984686 | 3.370877 | –0.952521 |
| 51 | 1 | 0 | –12.026201 | 3.828870 | 0.756488 |
| 52 | 1 | 0 | –13.054613 | 2.514124 | 0.167615 |

(A) HOMO (–7.13 eV)



(B) LUMO (–1.28 eV)

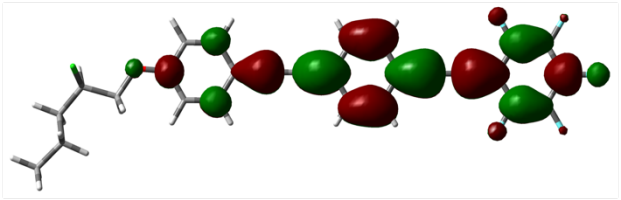


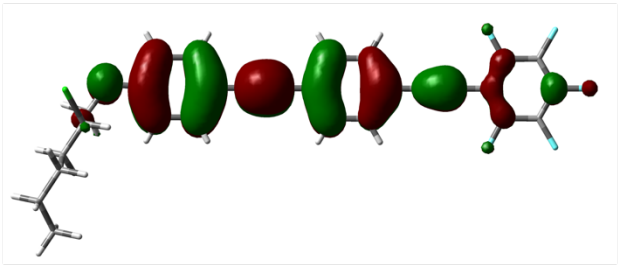
**Figure S6.** Molecular orbital diagrams for ***R*-2a** calculated by DFT//CAM-B3LYP/6-31G(d) level of theory with a CPCM model.

SCF Done: E(RCAM-B3LYP) = –2073.53937254 A.U.
Dipole moment (Debye): X= 4.5846 Y= 2.9555 Z= –2.3223 Tot= 5.9285

**Table S3.** Cartesian Coordinate for ***R*-2a** at the ground state

| Center Number | Atomic Number | Atomic Type | X | Y | Z |
|---|---|---|---|---|---|
| 1 | 17 | 0 | 10.352396 | –1.193607 | 1.220024 |
| 2 | 9 | 0 | –7.299001 | 2.497140 | 0.073603 |
| 3 | 9 | 0 | –9.988338 | 2.661606 | 0.141311 |
| 4 | 9 | 0 | –11.494278 | 0.398126 | 0.149968 |
| 5 | 9 | 0 | –7.601757 | –2.219026 | 0.021984 |
| 6 | 9 | 0 | –10.290061 | –2.040508 | 0.089788 |
| 7 | 8 | 0 | 7.687168 | –0.959569 | –0.360209 |
| 8 | 6 | 0 | 0.912056 | –0.405001 | –0.179592 |
| 9 | 6 | 0 | –2.685641 | –1.381769 | –0.114117 |
| 10 | 1 | 0 | –3.288598 | –2.283664 | –0.123631 |
| 11 | 6 | 0 | 2.120261 | –0.484529 | –0.211942 |
| 12 | 6 | 0 | –4.738359 | –0.035721 | –0.024181 |
| 13 | 6 | 0 | 5.559778 | –1.925071 | –0.335119 |
| 14 | 1 | 0 | 6.054281 | –2.890175 | –0.373183 |
| 15 | 6 | 0 | –0.512996 | –0.311618 | –0.140559 |
| 16 | 6 | 0 | –2.526079 | 1.032146 | –0.051191 |
| 17 | 1 | 0 | –3.004961 | 2.004857 | –0.011690 |
| 18 | 6 | 0 | 4.181127 | –1.833397 | –0.300436 |
| 19 | 1 | 0 | 3.580613 | –2.737228 | –0.311439 |
| 20 | 6 | 0 | –1.303941 | –1.471342 | –0.152333 |
| 21 | 1 | 0 | –0.825306 | –2.444089 | –0.191778 |
| 22 | 6 | 0 | –1.144442 | 0.941111 | –0.089346 |
| 23 | 1 | 0 | –0.541798 | 1.843128 | –0.079677 |
| 24 | 6 | 0 | –5.944382 | 0.042661 | 0.008164 |
| 25 | 6 | 0 | –3.313872 | –0.128516 | –0.063093 |
| 26 | 6 | 0 | 3.545778 | –0.579795 | –0.249541 |
| 27 | 6 | 0 | –9.394416 | 1.465259 | 0.112032 |
| 28 | 6 | 0 | –8.015070 | 1.368388 | 0.077060 |
| 29 | 6 | 0 | –10.164750 | 0.312364 | 0.116292 |
| 30 | 6 | 0 | –7.361353 | 0.133318 | 0.045310 |
| 31 | 6 | 0 | 6.342571 | –0.765141 | –0.320288 |
| 32 | 6 | 0 | 5.729642 | 0.487736 | –0.271967 |
| 33 | 1 | 0 | 6.312453 | 1.400429 | –0.262696 |
| 34 | 6 | 0 | –9.548357 | –0.929275 | 0.085582 |
| 35 | 6 | 0 | 8.544811 | 0.170486 | –0.311095 |
| 36 | 1 | 0 | 8.345515 | 0.757246 | 0.591098 |
| 37 | 1 | 0 | 8.377877 | 0.803593 | –1.192129 |
| 38 | 6 | 0 | 4.341339 | 0.570719 | –0.236534 |
| 39 | 1 | 0 | 3.868697 | 1.546867 | –0.198486 |
| 40 | 6 | 0 | –8.167783 | –1.008423 | 0.050835 |
| 41 | 6 | 0 | 10.955663 | 1.974774 | 0.365196 |
| 42 | 1 | 0 | 11.050822 | 1.616868 | 1.396588 |
| 43 | 1 | 0 | 9.985535 | 2.481533 | 0.296363 |
| 44 | 6 | 0 | 9.976759 | –0.321116 | –0.339839 |
| 45 | 1 | 0 | 10.069533 | –1.090979 | –1.107135 |
| 46 | 6 | 0 | 10.994933 | 0.785374 | –0.594752 |
| 47 | 1 | 0 | 11.993749 | 0.335621 | –0.584971 |
| 48 | 1 | 0 | 10.825648 | 1.137821 | –1.621242 |
| 49 | 6 | 0 | 12.067274 | 2.979066 | 0.067762 |
| 50 | 1 | 0 | 13.054611 | 2.514126 | 0.167612 |
| 51 | 1 | 0 | 12.026197 | 3.828875 | 0.756476 |
| 52 | 1 | 0 | 11.984687 | 3.370874 | –0.952531 |

(A) HOMO (–7.13 eV)



(B) LUMO (–1.28 eV)

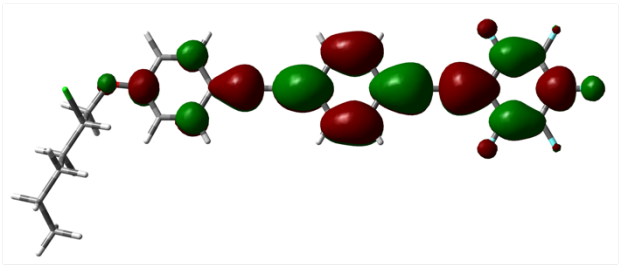


**Figure S7.** Molecular orbital diagrams for ***S*-2b** calculated by DFT//CAM-B3LYP/6-31+G(d) level of theory with a CPCM model.

SCF Done: E(RCAM-B3LYP) = –2112.82654341 A.U.
Dipole moment (Debye): X= 4.2556 Y= 3.0396 Z= –2.2053 Tot= 5.6756

**Table S4.** Cartesian Coordinate for ***S*-2b** at the ground state

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 17 | 0 | 9.410134 | –1.183812 | 1.505609 |
| 2 | 9 | 0 | –7.316651 | 2.525371 | –0.488144 |
| 3 | 9 | 0 | –7.818213 | –2.027486 | 0.675889 |
| 4 | 9 | 0 | –11.580113 | 0.758572 | 0.358149 |
| 5 | 9 | 0 | –9.986322 | 2.857103 | –0.311198 |
| 6 | 9 | 0 | –10.485982 | –1.681974 | 0.849557 |
| 7 | 8 | 0 | 7.445766 | –1.852296 | –0.800674 |
| 8 | 6 | 0 | –3.463274 | –0.278491 | –0.170199 |
| 9 | 6 | 0 | –0.683975 | –0.638475 | –0.342172 |
| 10 | 6 | 0 | –1.253759 | 0.626026 | –0.558785 |
| 11 | 1 | 0 | –0.611580 | 1.468177 | –0.793954 |
| 12 | 6 | 0 | –2.896693 | –1.543376 | 0.046436 |
| 13 | 1 | 0 | –3.539185 | –2.385278 | 0.281958 |
| 14 | 6 | 0 | 3.342706 | –1.173470 | –0.579146 |
| 15 | 6 | 0 | 0.730129 | –0.822687 | –0.428110 |
| 16 | 6 | 0 | 1.928862 | –0.981231 | –0.498961 |
| 17 | 6 | 0 | –1.525571 | –1.720269 | –0.038610 |
| 18 | 1 | 0 | –1.094440 | –2.701333 | 0.130281 |
| 19 | 6 | 0 | –6.073340 | 0.058882 | –0.003700 |
| 20 | 6 | 0 | 3.906130 | –2.447699 | –0.391774 |
| 21 | 1 | 0 | 3.258778 | –3.293963 | –0.185887 |
| 22 | 6 | 0 | –4.876716 | –0.095543 | –0.080853 |
| 23 | 6 | 0 | –2.624829 | 0.804264 | –0.474316 |
| 24 | 1 | 0 | –3.056237 | 1.785338 | –0.642977 |
| 25 | 6 | 0 | 4.199549 | –0.099740 | –0.843418 |
| 26 | 1 | 0 | 3.784053 | 0.892053 | –0.989574 |
| 27 | 6 | 0 | –8.077415 | 1.477089 | –0.157660 |
| 28 | 6 | 0 | –8.330159 | –0.817698 | 0.428744 |
| 29 | 6 | 0 | 6.119787 | –1.549690 | –0.732332 |
| 30 | 6 | 0 | 5.273972 | –2.632335 | –0.466517 |
| 31 | 1 | 0 | 5.712958 | –3.614246 | –0.323586 |
| 32 | 6 | 0 | –9.445754 | 1.659446 | –0.069677 |
| 33 | 6 | 0 | –10.260901 | 0.590844 | 0.271117 |
| 34 | 6 | 0 | –7.479441 | 0.237778 | 0.087995 |
| 35 | 6 | 0 | –9.700367 | –0.652428 | 0.521209 |
| 36 | 6 | 0 | 5.577196 | –0.277140 | –0.918773 |
| 37 | 1 | 0 | 6.202203 | 0.583290 | –1.123135 |
| 38 | 6 | 0 | 8.409091 | –0.829789 | –1.002462 |
| 39 | 1 | 0 | 8.081465 | –0.142076 | –1.789269 |
| 40 | 1 | 0 | 9.302634 | –1.346535 | –1.357219 |
| 41 | 6 | 0 | 8.734150 | –0.039042 | 0.257455 |
| 42 | 1 | 0 | 7.822432 | 0.351718 | 0.712972 |
| 43 | 6 | 0 | 9.712896 | 1.091338 | –0.030818 |
| 44 | 1 | 0 | 10.650528 | 0.668463 | –0.413440 |
| 45 | 1 | 0 | 9.274293 | 1.678224 | –0.847102 |
| 46 | 6 | 0 | 9.997994 | 2.006066 | 1.160161 |
| 47 | 1 | 0 | 10.411014 | 1.409076 | 1.980155 |
| 48 | 1 | 0 | 9.051687 | 2.428696 | 1.525429 |
| 49 | 6 | 0 | 10.969899 | 3.145418 | 0.837102 |
| 50 | 1 | 0 | 11.216193 | 3.662505 | 1.772307 |
| 51 | 1 | 0 | 11.912117 | 2.721134 | 0.465249 |
| 52 | 6 | 0 | 10.435629 | 4.166275 | –0.167419 |
| 53 | 1 | 0 | 10.262024 | 3.722136 | –1.153164 |
| 54 | 1 | 0 | 11.144333 | 4.990264 | –0.301455 |
| 55 | 1 | 0 | 9.487074 | 4.595345 | 0.177053 |