Supporting Information

Counter Ion Migration Driven by Light-Induced Intramolecular Charge Transfer

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Experiment section

General methods and materials

Unless otherwise mentioned, commercially available reagents were purchased from Sigma-Aldrich and Acros Organics without further purification. Solvent purification was according to Purification of Laboratory Chemicals. All reactions were carried out under Ar atmosphere and were monitored by thin layer chromatography (TLC) using pre-coated Merck silica gel 60 F254 alumina plates (0.25 mm). Visualization was accomplished using ultraviolet light (256 nm and 365 nm). Column chromatography was carried out using silica gel (230-400 mesh) supplied by Merck. $^1$H, $^{13}$C, $^{19}$F, $^{31}$P and $^{11}$B NMR spectra were recorded at 298 K on a Varian Unity 400 spectrometer; the chemical shifts (δ in ppm) are reported with DMSO-d$_6$ (δ 2.50 for $^1$H NMR and δ 39.52 for $^{13}$C NMR), CDCl$_3$ (δ 7.26 for $^1$H NMR and δ 77.06 for $^{13}$C NMR) or CD$_3$OD (δ 3.31 for $^1$H NMR and δ 49.00 for $^{13}$C NMR) as internal references. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, brs = broad singlet, m = multiplet. Single crystal X-ray diffraction data was collected on a Bruker D8 VENTURE diffractometer equipped with Oxford Cryostream 800+. High-resolution mass spectra (HRMS) were obtained using the electrospray ionization (ESI) method or fast atom bombardment (FAB) method with AB SCIEX QSTAR® XL.

Synthesis and characterization

Scheme S1. Synthesis route of C0[X].

$\text{N, N-diphenylpyridin-4-amine (N0).}$

A stirred solution of 4-bromopyridine hydrochloride (2.07 g, 10.64 mmol), diphenylamine (2.17 g, 12.82 mmol), Pd(OAc)$_2$ (110 mg, 0.491 mmol), rac-BINAP (310 mg, 0.498 mmol) and t-BuOK (3.21 g, 28.60 mmol) in toluene (90 mL) was heated at 120 °C for 18 h under argon atmosphere. After cooling to room temperature, the suspension was filtered through celite with EtOAc used as eluent. The combined organic solution was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (Hexane:EtOAc = 5:3) to afford 1a (1.416 g, 54%) as white solid. $^1$H NMR (400 MHz, DMSO-d$_6$, 298 K) δ (ppm): 8.17 (d, $J = 8.0$ Hz, 2H), 7.42 (t, $J = 20.0$, 8.0 Hz, 4H), 7.27-7.20 (m, 6H), 6.58 (d, $J = 8.0$ Hz, 2H).
4-(diphenylamino)-1-methylpyridin-1-ium iodide (C0[1]).

N0 (77 mg, 0.313 mmol) was dissolved in methyl iodide (10 mL). The reaction mixture was stirred for 16 h at room temperature and the product precipitated as a yellow solid. After filtration and washing with Et₂O, the crude product was then washed with CH₂Cl₂/toluene (1/1) three times to afford C0[1] (74 mg, 61%) as white solid. ¹H NMR (400 MHz, DMSO-d₆ 298 K) δ (ppm): 8.28 (d, J = 8.0 Hz, 2H), 7.58 (t, J = 16.0, 8.0 Hz, 4H), 7.53 - 7.44 (m, 6H), 6.75 (d, J = 8.0 Hz, 2H), 3.99 (s, 3H); ¹³C NMR (100 MHz, DMSO-d₆ 298 K) δ (ppm): 156.4, 144.3, 142.0, 130.7, 128.5, 127.3, 110.1, 44.7.

General procedure A for preparation of C0-2[X] by potassium-mediated counter anion exchange (X = PF₆, OTf, BPhCl).

A solution of K[X] salt in deionized water was added to the solution of C0-2[I] in dichloromethane. The reaction mixture was stirred at room temperature for 18 h. At the end of the reaction, the resulting mixture was poured into deionized water, and the aqueous layer was extracted with CH₂Cl₂ three times. The combined organic layer was concentrated under reduced pressure. The crude residue was then washing with CH₂Cl₂/toluene (1/1) three times to afford C0-2[X].

4-(diphenylamino)-1-methylpyridin-1-ium hexafluorophosphate(V) (C0[PF₆]).

Following general procedure A, compound C0[I] (150 mg, 0.386 mmol) was treated with potassium hexafluorophosphate (1208 mg, 6.56 mmol) in dichloromethane (20 mL) and deionized water (14 mL). After washing with CH₂Cl₂/toluene, C0[PF₆] was obtained as yellow solid (86 mg, 55%). ¹H NMR (400 MHz, DMSO-d₆ 298 K) δ (ppm): 8.26 (d, J = 8.0 Hz, 2H), 7.58 (t, J = 16.0, 8.0 Hz, 4H), 7.51 - 7.44 (m, 6H), 6.76 (d, J = 8.0 Hz, 2H), 3.98 (s, 3H); ¹³C NMR (100 MHz, DMSO-d₆ 298 K) δ (ppm): 156.4, 144.3, 142.1, 130.7, 128.6, 127.3, 110.2, 44.7; ¹⁹F NMR (376 MHz, DMSO-d₆ 298 K) δ (ppm): -69.6 (s, 3F), -71.5 (s, 3F); ³¹P NMR (64 MHz, DMSO-d₆ 298 K) δ (ppm): -143.1 (sept, 1P).

4-(diphenylamino)-1-methylpyridin-1-ium trifluoromethanesulfonate (C0[OTf]).

Following general procedure A, compound C0[I] (200 mg, 0.515 mmol) was treated with potassium trifluoromethanesulfonate (1648 mg, 8.76 mmol) in dichloromethane (50 mL) and deionized water (20 mL). After washing with CH₂Cl₂/toluene, C0[OTf] was obtained as yellow solid (108 mg, 51%). ¹H NMR (400 MHz, DMSO-d₆ 298 K) δ (ppm): 8.26 (d, J = 8.0 Hz, 2H), 7.60 - 7.46 (m, 10H), 6.76 (d, J = 8.0 Hz, 2H), 3.98 (s, 3H); ¹⁹F NMR (376 MHz, DMSO-d₆ 298 K) δ (ppm): -78.1 (s, 3F).
4-(diphenylamino)-1-methylpyridin-1-ium tetrakis(4-chlorophenyl)borate (CO[BPhCl]).

Following general procedure A, compound CO[I] (200 mg, 0.515 mmol) was treated with potassium tetrakis(4-chlorophenyl)borate (271 mg, 0.546 mmol) in dichloromethane (20 mL) and deionized water (10 mL). After washing with CH₂Cl₂/toluene, CO[BPhCl] was obtained as yellow solid (159 mg, 43%). ¹H NMR (400 MHz, DMSO-d₆, 298 K) δ (ppm): 8.25 (d, J = 8.0 Hz, 2H), 7.57 (t, J = 16.0, 8.0 Hz, 4H), 7.52-7.44 (m, 6H), 7.08-6.98 (m, 16H), 6.75 (d, J = 8.0 Hz, 2H), 3.97 (s, 3H); ¹¹B NMR (128 MHz, DMSO-d₆, 298 K) δ (ppm): -7.4 (s, 1B).

HRMS (ESI+): calcd. For C₁₈H₁₇N₂⁺ 261.1386, found 261.1392; HRMS (ESI−): calcd. For C₂₄H₁₆B₄Cl₄⁻ 455.0105, found 455.0102.

**Scheme S2.** Synthesis route of C1[X].

\[ N,N\text{-diphenyl-4-(pyridin-4-yl)aniline (N1).} \]

4-Bromotriphenylamine (1.00 g, 3.08 mmol), 4-pyridylboronic acid (0.455 g, 3.70 mmol), Pd(PPh₃)₄ (0.286 g, 0.247 mmol) and K₂CO₃ (1.28 g, 9.26 mmol) were added to the solution of 1,4-dioxane (60 mL) and water (3 mL). The mixture was heated at 110 °C for 18 h under argon atmosphere. After cooling to room temperature, the suspension was filtered through celite with EtOAc used as eluent. The combined organic solution was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (Hexane:EtOAc = 5:2) to afford N1 (0.676 g, 68%) as yellow solid. ¹H NMR (400 MHz, CDCl₃, 298 K) δ (ppm): 8.62 (brs, 2H), 7.52 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.29 (t, J = 16.0, 8.0 Hz, 4H), 7.16-7.13 (m, 6H), 7.08 (t, J = 16.0, 8.0 Hz, 2H).

4-(4-(diphenylamino)phenyl)-1-methylpyridin-1-ium iodide (C1[I]).

N1 (100 mg, 0.310 mmol) was dissolved in methyl iodide (7 mL). The reaction mixture was stirred for 16 h at room temperature and the product precipitated as a yellow solid. After filtration and washing with Et₂O, the crude product was then washing with CH₂Cl₂/toluene (1/1) three times to afford C1[I] (105 mg, 73%) as yellow solid. ¹H NMR (400 MHz, DMSO-d₆, 298 K) δ (ppm): 8.84 (d, J = 8.0 Hz, 2H), 8.34 (d, J = 8.0 Hz, 2H), 7.99 (d, J = 8.0 Hz, 2H), 7.42 (t, J = 16.0, 8.0 Hz, 4H), 7.24-7.17 (m, 6H), 6.97 (d, J = 8.0 Hz, 2H), 4.25 (s, 3H).
4-(4-(diphenylamino)phenyl)-1-methylpyridin-1-ium hexafluorophosphate(V) (C1[PF₆]).

Following general procedure A, compound C1[I] (100 mg, 0.215 mmol) was treated with potassium hexafluorophosphate (680 mg, 3.69 mmol) in dichloromethane (22 mL) and deionized water (10 mL). After washing with CH₂Cl₂/toluene, C1[PF₆] was obtained as yellow solid (65 mg, 63%). ¹H NMR (400 MHz, DMSO-d₆, 298 K) δ (ppm): 8.84 (d, J = 8.0 Hz, 2H), 8.34 (d, J = 8.0 Hz, 2H), 7.99 (d, J = 8.0 Hz, 2H), 7.42 (t, J = 16.0, 8.0 Hz, 4H), 7.24-7.18 (m, 6H), 6.97 (d, J = 8.0 Hz, 2H), 4.25 (s, 3H); ¹⁹F NMR (376 MHz, DMSO-d₆, 298 K) δ (ppm): -64.8 (s, 3F), -66.7 (s, 3F); ³¹P NMR (64 MHz, DMSO-d₆, 298 K) δ (ppm): -138.4 (sept, 1P).

4-(4-(diphenylamino)phenyl)-1-methylpyridin-1-ium trifluoromethanesulfonate (C1[OTf]).

Following general procedure A, compound C1[I] (200 mg, 0.431 mmol) was treated with potassium trifluoromethanesulfonate (1380 mg, 7.33 mmol) in dichloromethane (50 mL) and deionized water (20 mL). After washing with CH₂Cl₂/toluene, C1[OTf] was obtained as yellow solid (147 mg, 70%). ¹H NMR (400 MHz, DMSO-d₆, 298 K) δ (ppm): 8.83 (d, J = 8.0 Hz, 2H), 8.33 (d, J = 8.0 Hz, 2H), 7.99 (d, J = 8.0 Hz, 2H), 7.42 (t, J = 16.0, 8.0 Hz, 4H), 7.25-7.17 (m, 6H), 6.97 (d, J = 8.0 Hz, 2H), 4.24 (s, 3H); ¹⁹F NMR (376 MHz, DMSO-d₆, 298 K) δ (ppm): -78.1 (s, 3F).

4-(4-(diphenylamino)phenyl)-1-methylpyridin-1-ium tetrakis(4-chlorophenyl)borate (C1[BPhCl]).

Following general procedure A, compound C1[I] (100 mg, 0.215 mmol) was treated with potassium tetrakis(4-chlorophenyl)borate (115 mg, 0.232 mmol) in dichloromethane (23 mL) and deionized water (10 mL). After washing with CH₂Cl₂/toluene, C1[BPhCl] was obtained as orange solid (116 mg, 68%). ¹H NMR (400 MHz, DMSO-d₆, 298 K) δ (ppm): 8.84 (d, J = 4.0 Hz, 2H), 8.34 (d, J = 4.0 Hz, 2H), 7.99 (d, J = 4.0 Hz, 2H), 7.42 (t, J = 16.0, 8.0 Hz, 4H), 7.24-7.18 (m, 6H), 7.08-6.96 (m, 18H), 4.24 (s, 3H); ¹¹B NMR (128 MHz, DMSO-d₆, 298 K) δ (ppm): -7.4 (s, 1B). HRMS (ESI+): calcd. For C₂₅H₂₁N₂+ 337.1699, found 337.1706; HRMS (ESI−): calcd. For C₂₅H₁₆BCl₄ 455.0105, found 455.0101.

Scheme S3. Synthesis route of C2[X].
N, N-diphenyl-4’-(pyridin-4-yl)-[1,1'-biphenyl]-4-amine (N2).

4-Bromo-4’-(diphenylamino)biphenyl (700 mg, 1.75 mmol), 4-pyridylboronic acid (645 mg, 5.25 mmol), Pd(PPh₃)₄ (162 mg, 0.140 mmol) and Cs₂CO₃ (1710 mg, 5.25 mmol) were dissolved in anhydrous THF (60 mL). The mixture was heated at 80 °C for 18 h under argon atmosphere. After cooling to room temperature, the suspension was filtered through celite with EtOAc used as eluent. The combined organic solution was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (Hexane:EtOAc = 5:2) to afford N2 (495 mg, 71%) as yellow solid. ¹H NMR (400 MHz, CDCl₃, 298 K) δ (ppm): 8.71 (brs, 2H), 7.69 (brs, 4H), 7.57 (brs, 2H), 7.52-7.49 (m, 2H), 7.30-7.25 (m, 4H), 7.16-7.13 (m, 6H), 7.05 (t, J = 16.0, 8.0 Hz, 2H).

4-(4’-(diphenylamino)-[1,1'-biphenyl]-4-yl)-1-methylpyridin-1-ium iodide (C2[I]).

N2 (124 mg, 0.311 mmol) was dissolved in methyl iodide (7 mL). The reaction mixture was stirred for 16 h at room temperature and the product precipitated as a yellow solid. After filtration and washing with Et₂O, the crude product was then washing with CH₂Cl₂/toluene (1/1) three times to afford C2[I] (111 mg, 66%) as red solid. ¹H NMR (400 MHz, DMSO-d₆, 298 K) δ (ppm): 9.00 (d, J = 8.0 Hz, 2H), 8.56 (d, J = 8.0 Hz, 2H), 7.93 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H), 7.38-7.33 (m, 4H), 7.14-7.03 (m, 8H), 4.33 (s, 3H).

4-(4’-(diphenylamino)-[1,1'-biphenyl]-4-yl)-1-methylpyridin-1-ium hexafluorophosphate(V) (C2[PF₆]).

Following general procedure A, compound C2[I] (170 mg, 0.315 mmol) was treated with potassium hexafluorophosphate (985 mg, 5.35 mmol) in dichloromethane (45 mL) and deionized water (20 mL). After washing with CH₂Cl₂/toluene, C2[PF₆] was obtained as yellow solid (132 mg, 75%). ¹H NMR (400 MHz, DMSO-d₆, 298 K) δ (ppm): 8.98 (d, J = 8.0 Hz, 2H), 8.17 (d, J = 8.0 Hz, 2H), 7.92 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H), 7.37-7.34 (m, 4H), 7.13-7.05 (m, 8H), 4.32 (s, 3H); ¹⁹F NMR (376 MHz, DMSO-d₆, 298 K) δ (ppm): -69.6 (s, 3F), -71.4 (s, 3F); ³¹P NMR (64 MHz, DMSO-d₆, 298 K) δ (ppm): -143.1 (sept, 1F).

4-(4’-(diphenylamino)-[1,1'-biphenyl]-4-yl)-1-methylpyridin-1-ium trifluoromethanesulfonate (C2[OTf]).

Following general procedure A, compound C2[I] (121 mg, 0.224 mmol) was treated with potassium trifluoromethanesulfonate (715 mg, 3.80 mmol) in dichloromethane (50 mL) and deionized water (20 mL). After washing with CH₂Cl₂/toluene, C2[OTf] was obtained as yellow solid (98 mg, 78%). ¹H NMR (400 MHz, DMSO-d₆, 298 K) δ (ppm): 8.98 (d, J = 8.0 Hz, 2H), 8.17 (d, J = 8.0 Hz, 2H), 7.92 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H), 7.38-7.34 (m, 4H), 7.13-7.04 (m, 8H), 4.32 (s, 3H); ¹⁹F NMR (376 MHz, DMSO-d₆, 298 K) δ (ppm): -78.1 (s, 3F).
4-(4'-(diphenylamino)-[1,1’-biphenyl]-4-yl)-1-methylpyridin-1-ium tetrakis(4-chlorophenyl)borate (C2[BPhCl]).

Following general procedure A, compound C2[I] (120 mg, 0.222 mmol) was treated with potassium tetrakis(4-chlorophenyl)borate (120 mg, 0.242 mmol) in dichloromethane (25 mL) and deionized water (15 mL). After washing with CH2Cl2/toluene, C2[BPhCl] was obtained as orange solid (130 mg, 67%). 1H NMR (400 MHz, DMSO-d6, 298 K) δ (ppm): 8.97 (d, J = 8.0 Hz, 2H), 8.53 (d, J = 8.0 Hz, 2H), 8.16 (d, J = 8.0 Hz, 2H), 7.91 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H), 7.37-7.33 (m, 4H), 7.13-7.04 (m, 16H), 7.00-6.99 (m, 8H), 4.31 (s, 3H); 13C NMR (100 MHz, DMSO-d6, 298 K) δ (ppm): 153.6, 151.1, 145.6, 144.2, 129.9, 129.5, 126.0, 125.2, 124.4, 122.5, 119.5, 59.1, 50.3, 29.8, 21.6. LRMS (FAB-): calcd. For C27H39N2O3S 458.1664, found 458.2; HRMS (FAB+): calcd. For C27H39N2O3S+ 459.1737, found 459.1741.

Scheme S4. Synthesis route of Z1-2Bs.

4-(4-(4-(diphenylamino)phenyl)pyridin-1-ium-1-yl)butane-1-sulfonate (Z1Bs).

N1 (100 mg, 0.310 mmol) was dissolved in dried toluene (3 mL). After the mixture was stirred for 20 min at room temperature, 1,4-butanesultone (Bs, 43 mg, 0.310 mmol) was added drop by drop within 30 min. Then, the reaction mixture was heated at 120 °C for 48 h under argon atmosphere. After cooling to room temperature, the resultant precipitate was washed with toluene to afford Z1Bs as yellow solid. The purified Z1Bs was collected by subsequently washing with toluene (6 mL × 3) and diethyl ether (6 mL × 3) and dried under vacuum. Its color was yellow, and the yield was 33%. 1H NMR (400 MHz, DMSO-d6, 298 K) δ (ppm): 8.93 (d, J = 8.0 Hz, 2H), 8.34 (d, J = 8.0 Hz, 2H), 7.98 (d, J = 8.0 Hz, 2H), 7.41 (t, J = 16.0, 8.0 Hz, 4H), 7.23-7.16 (m, 6H), 6.94 (d, J = 8.0 Hz, 2H), 4.53-4.49 (m, 2H), 2.46-2.44 (m, 2H), 2.02-1.97 (m, 2H), 1.61-1.53 (m, 2H); 13C NMR (100 MHz, DMSO-d6, 298 K) δ (ppm): 153.6, 151.1, 145.6, 144.2, 129.9, 129.5, 126.0, 125.2, 124.4, 122.5, 119.5, 59.1, 50.3, 29.8, 21.6. LRMS (FAB-): calcd. For C27H26N3O5S+ 459.1737, found 459.1741.
4-(4′-(diphenylamino)-[1,1′-biphenyl]-4-yl)pyridin-1-ium-1-yl)butane-1-sulfonate (Z2Bs).

N2 (100 mg, 0.251 mmol) was dissolved in dried toluene (3 mL). After the mixture was stirred for 20 min at room temperature, 1,4-butanesultone (Bs, 35 mg, 0.251 mmol) was added drop by drop within 30 min. Then, the reaction mixture was heated at 120 °C for 48 h under argon atmosphere. After cooling to room temperature, the resultant precipitate was washed with toluene to afford Z2Bs as yellow solid. The purified Z2Bs was collected by subsequently washing with toluene (6 mL × 3) and diethyl ether (6 mL × 3) and dried under vacuum. Its color was yellow, and the yield was 31%. 1H NMR (400 MHz, DMSO-d6, 298 K) δ (ppm): 9.06 (d, J = 8.0 Hz, 2H), 8.53 (d, J = 8.0 Hz, 2H), 8.15 (d, J = 8.0 Hz, 2H), 7.88 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H), 7.32 (t, J = 16.0, 8.0 Hz, 4H), 7.10-7.01 (m, 8H), 4.59-4.55 (m, 2H), 2.45-2.42 (m, 2H), 2.05-1.97 (m, 2H), 1.62-1.54 (m, 2H).

Scheme S5. Synthesis route of t-C2[X].

4'-bromo-N,N-bis(4-(tert-butyl)phenyl)-[1,1′-biphenyl]-4-amine.

A stirred solution of 4,4’-Dibromobiphenyl (3.33 g, 10.66 mmol), bis(4-tert-butylphenyl)amine (1.00 g, 3.55 mmol), tris(dibenzylideneacetone)dipalladium(0) (0.048 g, 0.015 mmol), 1,1′-bis(diphenylphosphine)ferrocene (0.048 g, 0.085 mmol) and sodium tert-butoxide (0.48 g, 4.98 mmol) in toluene (60 mL) was heated at 120 °C for 18 h under argon atmosphere. After cooling to room temperature, the resulting mixture was poured into a large amount of water for extraction with EtOAc. The combined organic solution was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (Hexane:CH3Cl = 10:1) to afford the desirable pure product (0.783 g, 43%) as white solid. 1H NMR (400 MHz, CDCl3, 298 K) δ (ppm): 7.53 (d, J = 8.0 Hz, 2H), 7.42 (t, J = 16.0, 8.0 Hz, 4H), 7.30 (d, J = 8.0 Hz, 4H), 7.13-7.07 (m, 6H), 1.34 (s, 18H); 13C NMR (100 MHz, CDCl3, 298 K) δ (ppm): 147.8, 145.9, 144.7, 139.6, 132.6, 131.7, 128.0, 127.3, 126.0, 124.1, 122.7, 120.6, 34.2, 31.4.
$N, N$-bis(4-(tert-butyl)phenyl)-4'-[pyridin-4-yl]-[1,1'-biphenyl]-4-amine ($\text{t-N2}$).

$4'$-bromo-N, $N$-bis(4-(tert-butyl)phenyl)-[1,1'-biphenyl]-4-amine (378 mg, 0.738 mmol), 4-pyridyldiboronic acid (109 mg, 0.886 mmol), Pd($\text{PPh}_3)_4$ (69 mg, 0.059 mmol) and Cs$_2$CO$_3$ (289 mg, 0.886 mmol) were dissolved in anhydrous THF (20 mL). The mixture was heated at 80 °C for 18 h under argon atmosphere. After cooling to room temperature, the suspension was filtered through celite with EtOAc used as eluent. The combined organic solution was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (Hexane:EtOAc = 2:1) to afford $\text{t-N2}$ (237 mg, 63%) as yellow solid. $^1$H NMR (400 MHz, CDCl$_3$, 298 K) $\delta$ (ppm): 8.68 (brs, 2H), 7.69 (s, 4H), 7.55 (d, $J = 8.0$ Hz, 2H), 7.50 (d, $J = 8.0$ Hz, 2H), 7.30 (d, $J = 8.0$ Hz, 4H), 7.14 (d, $J = 8.0$ Hz, 2H), 7.09 (d, $J = 8.0$ Hz, 4H), 1.35 (s, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$, 298 K) $\delta$ (ppm): 150.1, 147.9, 147.7, 145.9, 144.7, 141.5, 135.9, 132.7, 127.4, 127.2, 127.0, 126.0, 124.2, 122.6, 121.3, 34.2, 31.3.

$4'$-(4'-bis(4-(tert-butyl)phenyl)amino)-[1,1'-biphenyl]-4-yl)-1-methylpyridin-1-ium iodide ($\text{t-C2[I]}$).

$\text{t-N2}$ (85 mg, 0.166 mmol) was dissolved in methyl iodide (4 mL). The reaction mixture was stirred for 18 h at room temperature and the product precipitated as orange solid. After filtration and washing with EtOAc, the crude product was then washing with CH$_2$Cl$_2$/toluene (1/2) two times to afford $\text{t-C2[I]}$ (63 mg, 58%) as orange solid. $^1$H NMR (400 MHz, DMSO-$d_6$, 298 K) $\delta$ (ppm): 8.96 (d, $J = 8.0$ Hz, 2H), 8.52 (d, $J = 8.0$ Hz, 2H), 8.14 (d, $J = 8.0$ Hz, 2H), 7.87 (d, $J = 8.0$ Hz, 2H), 7.68 (d, $J = 8.0$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 4H), 7.00 (d, $J = 8.0$ Hz, 4H), 6.96 (d, $J = 8.0$ Hz, 2H), 4.30 (s, 3H), 1.26 (s, 18H); $^{13}$C NMR (100 MHz, DMSO-$d_6$, 298 K) $\delta$ (ppm): 153.6, 148.0, 146.1, 145.4, 144.0, 143.1, 131.3, 130.7, 128.6, 127.7, 126.8, 126.4, 124.4, 123.5, 121.3, 46.9, 34.1, 31.1.

$4'$-(4'-bis(4-(tert-butyl)phenyl)amino)-[1,1'-biphenyl]-4-yl)-1-methylpyridin-1-ium trifluoromethanesulfonate ($\text{t-C2[OTf]}$).

Following general procedure A, compound $\text{t-C2[I]}$ (33 mg, 0.051 mmol) was treated with potassium trifluoromethanesulfonate (163 mg, 0.866 mmol) in dichloromethane (16 mL) and deionized water (8 mL). After washing with CH$_2$Cl$_2$/toluene (1/5) two times, $\text{t-C2[OTf]}$ was obtained as orange solid (24 mg, 70%). $^1$H NMR (400 MHz, DMSO-$d_6$, 298 K) $\delta$ (ppm): 8.95 (d, $J = 8.0$ Hz, 2H), 8.50 (d, $J = 8.0$ Hz, 2H), 8.13 (d, $J = 8.0$ Hz, 2H), 7.87 (d, $J = 8.0$ Hz, 2H), 7.68 (d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 4H), 7.00 (d, $J = 8.0$ Hz, 4H), 6.95 (d, $J = 8.0$ Hz, 2H), 4.30 (s, 3H), 1.26 (s, 18H); $^{13}$C NMR (100 MHz, DMSO-$d_6$, 298 K) $\delta$ (ppm): 153.6, 148.1, 146.1, 145.4, 144.1, 143.1, 131.3, 130.7, 128.6, 127.7, 126.8, 126.4, 124.4, 123.5, 121.3, 46.9, 34.1, 31.2; $^{19}$F NMR (376 MHz, DMSO-$d_6$, 298 K) $\delta$ (ppm): -73.4 (s, 3F).
Scheme S6. Synthesis route of t-Z2Bs.

4-(4'-[(bis(4-(tert-butyl)phenyl)amino)-[1,1'-biphenyl]-4-yl]pyridin-1-ium-1-yl)butane-1-sulfonate (t-Z2Bs)

t-N2 (51 mg, 0.10 mmol) was dissolved in 1,4-butanesultone (Bs, 3mL). Then, the reaction mixture was heated at 120 °C for 4h under argon atmosphere. After cooling to room temperature, the resultant precipitate was washed with Et₂O to afford t-Z2Bs as orange solid. The purified t-Z2Bs was collected by subsequently washing with toluene (2 mL x 3) and dried under vacuum. Its color was orange, and the yield was 36%. \(^1\)H NMR (400 MHz, CD₃OD, 298 K) \(\delta\) (ppm): 8.93 (d, \(J = 8.0\) Hz, 2H), 8.43 (d, \(J = 8.0\) Hz, 2H), 7.88 (d, \(J = 8.0\) Hz, 2H), 7.63 (d, \(J = 8.0\) Hz, 2H), 7.36 (d, \(J = 8.0\) Hz, 4H), 7.09-7.03 (m, \(J = 8.0\) Hz, 6H), 4.67-4.63 (m, 2H), 2.92-2.88 (m, 2H), 2.26-2.19 (m, 2H), 1.89-1.83 (m, 2H), 1.33 (s, 18H).
NMR analysis

Figure S1. Scaled stacked $^1$H NMR spectra of $K[BPhCl]$, $C0[I]$ and $C0[BPhCl]$ in DMSO-$d_6$.

Figure S2. Scaled stacked $^1$H NMR spectra of $K[BPhCl]$, $C1[I]$ and $C1[BPhCl]$ in DMSO-$d_6$. 
Figure S3. Scaled stacked $^1$H NMR spectra of $\text{K[BPhCl]}$, $\text{C}_2[\text{I}]$ and $\text{C}_2[\text{BPhCl}]$ in DMSO-$d_6$.

Figure S4. Scaled stacked $^{19}$F NMR spectra of $\text{t-C}_2[\text{I}]$ and $\text{t-C}_2[\text{OTf}]$ in DMSO-$d_6$. 

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Figure S5. $^1$H NMR spectrum of compound N0.

Figure S6. $^1$H NMR spectrum of compound C0[1].
Figure S7. $^{13}$C NMR spectrum of compound C0[1].

Figure S8. $^1$H NMR spectrum of compound C0[PFS₆].
Figure S9. $^{13}$C NMR spectrum of compound C0[PF$_6$].

Figure S10. $^{19}$F NMR spectrum of compound C0[PF$_6$].
Figure S11. $^{31}$P NMR spectrum of compound C0[P$_6$F$_6$].

Figure S12. $^1$H NMR spectrum of compound C0[OTf].
Figure S13. $^{19}$F NMR spectrum of compound C0[OTf].

Figure S14. $^1$H NMR spectrum of compound C0[BPhCl].
**Figure S15.** $^1$B NMR spectrum of compound $\text{C}_0[\text{BPhCl}]$.

**Figure S16.** $^1$H NMR spectrum of compound $\text{K}[\text{BPhCl}]$. 
Figure S17. $^1$H NMR spectrum of compound N1.

Figure S18. $^1$H NMR spectrum of compound C1[I].
Figure S19. $^1$H NMR spectrum of compound C1[Pf$_6$].

Figure S20. $^{19}$F NMR spectrum of compound C1[Pf$_6$].
Figure S21. $^{31}$P NMR spectrum of compound C1[P$_6$F$_6$].

Figure S22. $^1$H NMR spectrum of compound C1[OTf].
Figure S23. $^{19}$F NMR spectrum of compound C1[OTf].

Figure S24. $^1$H NMR spectrum of compound C1[BPhCl].
Figure S25. $^{11}$B NMR spectrum of compound C1[BPhCl].

Figure S26. $^1$H NMR spectrum of compound N2.
Figure S27. $^1$H NMR spectrum of compound C2[1].

Figure S28. $^1$H NMR spectrum of compound C2[PF$_6$].
Figure S29. $^{19}$F NMR spectrum of compound C2[PF$_6$].

Figure S30. $^{31}$P NMR spectrum of compound C2[PF$_6$].
**Figure S31.** $^1$H NMR spectrum of compound C2[OTf].

**Figure S32.** $^{19}$F NMR spectrum of compound C2[OTf].
Figure S33. $^1$H NMR spectrum of compound C2[BPhCl].

Figure S34. $^{11}$B NMR spectrum of compound C2[BPhCl].
Figure S35. $^1$H NMR spectrum of compound Z1Bs.

Figure S36. $^{13}$C NMR spectrum of compound Z1Bs.
Figure S37. $^1$H NMR spectrum of compound Z2Bs.

Figure S38. $^{13}$C NMR spectrum of compound Z2Bs.
Figure S39. $^1$H NMR spectrum of 4'-bromo-N,N-bis(4-(tert-butyl)phenyl)-[1,1'-biphenyl]-4-amine.

Figure S40. $^{13}$C NMR spectrum of 4'-bromo-N,N-bis(4-(tert-butyl)phenyl)-[1,1'-biphenyl]-4-amine.
Figure S41. $^1$H NMR spectrum of compound $t$-N2.

Figure S42. $^{13}$C NMR spectrum of compound $t$-N2.
Figure S43. $^1$H NMR spectrum of compound $t$-C2[1].

Figure S44. $^{13}$C NMR spectrum of compound $t$-C2[1].
Figure S45. $^1$H NMR spectrum of compound $t$-C2[OTf].

Figure S46. $^{13}$C NMR spectrum of compound $t$-C2[OTf].
Figure S47. $^{19}$F NMR spectrum of compound $\text{t-C2[OTf]}$.

Figure S48. $^1$H NMR spectrum of compound $\text{t-Z2Bs}$.
**Crystallization data**

Single crystals of title compounds were achieved from slow evaporation of hexanes/dichloromethane solution at room temperature. Single crystal X-ray diffraction data were obtained from a Bruker D8 VENTURE single-crystal XRD equipped with Oxford Cryostream 800+ at a temperature of 200 K. Structures of the crystals were solved by direct methods using the SHELXS-97 software. None-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations on $F^2$ using SHELXL-97, while the hydrogen atoms were introduced at calculated positions and refined in the riding mode.

Structures of title compounds have been submitted to the Cambridge Crystallographic Data Centre, with the deposition number CCDC 2000196 (C0[PF$_6$]), 2000195 (C1[PF$_6$]), 2000197 (C2[PF$_6$]), 2000194 (C0[OTf]), 2000157 (C1[OTf]), 2000193 (C2[OTf]), 2000192 (C1[I]) and 2000125 (C2[I]), respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via http://www.ccdc.cam.ac.uk/structures. Drawings were produced using Mercury.

![Figure S49](image-url). The 50 % probability level of the crystal structure of C0[PF$_6$] (a) and C0[OTf] (b).
| Identification code | **C0[PF₆]** | **C0[OTf]** |
|---------------------|-------------|-------------|
| **Empirical formula** | C₁₉H₁₇F₆N₂P | C₁₉H₁₇F₃N₂O₃S |
| **Formula weight** | 406.30 | 410.40 |
| **Temperature** | 200(2) K | 200(2) K |
| **Wavelength** | 1.54178 Å | 1.54178 Å |
| **Crystal system** | Orthorhombic | Monoclinic |
| **Space group** | P2₁2₁2₁ | P2₁/n |
| **Unit cell dimensions** | a = 5.85500(10) Å, α = 90° | a = 8.9362(2) Å, α = 90° |
| | b = 12.9566(3) Å, β = 90° | b = 21.7344(4) Å, β = 101.8840(6)° |
| | c = 24.0021(5) Å, γ = 90° | c = 9.9022(2) Å, γ = 90° |
| **Volume** | 1820.82(6) Å³ | 1882.01(7) Å³ |
| **Z** | 4 | 4 |
| **Density (calculated)** | 1.482 Mg/m³ | 1.448 Mg/m³ |
| **Absorption coefficient** | 1.943 mm⁻¹ | 2.007 mm⁻¹ |
| **F(000)** | 832 | 848 |
| **Crystal size** | 0.298 x 0.195 x 0.151 mm³ | 0.344 x 0.195 x 0.050 mm³ |
| **Theta range for data collection** | 3.877 to 74.997°. | 4.068 to 74.946°. |
| **Index ranges** | -7 ≤ h ≤ 6, -14 ≤ k ≤ 16, -30 ≤ l ≤ 29 | -9 ≤ h ≤ 11, -26 ≤ k ≤ 27, -12 ≤ l ≤ 11 |
| **Reflections collected** | 9530 | 9778 |
| **Completeness to theta = 67.679°** | 99.2 % | 99.4 % |
| **Absorption correction** | Semi-empirical from equivalents | Semi-empirical from equivalents |
| **Max. and min. transmission** | 0.7539 and 0.6155 | 0.7539 and 0.5954 |
| **Refinement method** | Full-matrix least-squares on F² | Full-matrix least-squares on F² |
| **Data / restraints / parameters** | 3716 / 0 / 245 | 3845 / 0 / 276 |
| **Goodness-of-fit on F²** | 1.067 | 1.071 |
| **Final R indices [1>2sigma(I)]** | R1 = 0.0363, wR2 = 0.0981 | R1 = 0.0628, wR2 = 0.1678 |
| **R indices (all data)** | R1 = 0.0369, wR2 = 0.0990 | R1 = 0.0661, wR2 = 0.1737 |
| **Absolute structure parameter** | 0.076(8) | n/a |
| **Extinction coefficient** | n/a | n/a |
| **Largest diff. peak and hole** | 0.216 and -0.240 e.Å⁻³ | 0.707 and -0.480 e.Å⁻³ |
Figure S50. The 50 % probability level of the crystal structure of C1[I] (a), C1[PF₆] (b) and C1[OTf] (c).
| Identification code | C1[I] | C1[PF6] | C1[OTf] |
|--------------------|-------|---------|---------|
| **Empirical formula** | C₉H₁₂IN₂ | C₉H₁₂F₃N₂P | C₉H₁₂F₃N₂O₃S |
| **Formula weight** | 464.33 | 482.40 | 486.50 |
| **Temperature** | 200(2) K | 200(2) K | 200(2) K |
| **Wavelength** | 0.71073 Å | 1.54178 Å | 1.54178 Å |
| **Crystal system** | Orthorhombic | Monoclinic | Monoclinic |
| **Space group** | Pbc a | P2₁/n | P2₁/c |
| **Unit cell dimensions** | a = 16.1726(6) Å, α = 90° | b = 21.72(4) Å, β = 90° | c = 22.1172(9) Å, γ = 90° |
| | b = 11.2172(4) Å, β = 90° | b = 26.8386(9) Å, β = 99.3508(7)° | b = 40.3918(8) Å, β = 90.6505(6)° |
| | c = 22.3203(9) Å, γ = 90° | c = 14.0594(5) Å, γ = 90° | c = 11.2716(2) Å, γ = 90° |
| **Volume** | 4049.2(3) Å³ | 2218.43(13) Å³ | 4665.18(15) Å³ |
| **Z** | 8 | 4 | 8 |
| **Density (calculated)** | 1.523 Mg/m³ | 1.444 Mg/m³ | 1.385 Mg/m³ |
| **Absorption coefficient** | 1.592 mm⁻¹ | 1.692 mm⁻¹ | 1.712 mm⁻¹ |
| **F(000)** | 1856 | 992 | 2016 |
| **Theta range for data collection** | 2.217 to 30.000° | 3.586 to 74.981° | 4.072 to 74.989° |
| **Index ranges** | -22 ≤ h ≤ 22, -13 ≤ k ≤ 15 | -7 ≤ h ≤ 7, -32 ≤ k ≤ 33, -17 ≤ l ≤ 15 | -12 ≤ h ≤ 11, -50 ≤ k ≤ 48, -14 ≤ l ≤ 14 |
| **Reflections collected** | 26153 | 13253 | 29289 |
| **Completeness to theta** | 99.9 % | 99.7 % | 99.9 % |
| **Absorption correction** | Semi-empirical from equivalents | Semi-empirical from equivalents | Semi-empirical from equivalents |
| **Max. and min. transmission** | 0.7460 and 0.5790 | 0.7539 and 0.6214 | 0.7539 and 0.5097 |
| **Refinement method** | Full-matrix least-squares on F² | Full-matrix least-squares on F² | Full-matrix least-squares on F² |
| **Data / restraints / parameters** | 5899 / 0 / 245 | 4554 / 0 / 299 | 9556 / 0 / 615 |
| **Goodness-of-fit on F²** | 1.041 | 1.028 | 1.051 |
| **Final R indices [I>2sigma(I)]** | R1 = 0.0308, wR2 = 0.0751 | R1 = 0.0417, wR2 = 0.1096 | R1 = 0.0569, wR2 = 0.1570 |
| **R indices (all data)** | R1 = 0.0457, wR2 = 0.0854 | R1 = 0.0438, wR2 = 0.1117 | R1 = 0.0621, wR2 = 0.1629 |
| **Absolute structure parameter** | n/a | n/a | n/a |
| **Extinction coefficient** | 0.413 and -1.084 e Å⁻³ | 0.460 and -0.322 e Å⁻³ | 0.503 and -1.203 e Å⁻³ |
Figure S51. The 50 % probability level of the crystal structure of C2[I] (a), C2[PF6] (b) and C2[OTf] (c).
| Identification code | C2[I] | C2[P6] | C2[OTf] |
|---------------------|-------|--------|---------|
| **Empirical formula** | C$_{30}$H$_{25}$IN$_{2}$ | C$_{30}$H$_{25}$F$_{6}$N$_{2}$P | C$_{31}$H$_{25}$F$_{3}$N$_{2}$O$_{3}$S |
| **Formula weight** | 558.43 | 558.49 | 562.59 |
| **Temperature** | 200(2) K | 200(2) K | 200(2) K |
| **Wavelength** | 1.54178 Å | 1.54178 Å | 1.54178 Å |
| **Crystal system** | Orthorhombic | Monoclinic | Monoclinic |
| **Space group** | Pbcn | P2$_1$/c | P2$_1$/c |
| **Unit cell dimensions** | $a = 30.4682(9)$ Å, $\alpha = 90^\circ$. | $a = 21.5557(5)$ Å, $\alpha = 90^\circ$. | $a = 21.2770(5)$ Å, $\alpha = 90^\circ$. |
| | $b = 10.0646(3)$ Å, $\beta = 90^\circ$. | $b = 10.4015(2)$ Å, $\beta = 94.3480(9)^\circ$. | $b = 11.0088(3)$ Å, $\beta = 92.7839(9)^\circ$. |
| | $c = 16.1931(5)$ Å, $\gamma = 90^\circ$. | $c = 11.9634(2)$ Å, $\gamma = 90^\circ$. | $c = 11.1794(3)$ Å, $\gamma = 90^\circ$. |
| **Volume** | 4965.6(3) Å$^3$ | 2674.61(9) Å$^3$ | 2615.51(12) Å$^3$ |
| **Z** | 8 | 4 | 4 |
| **Density (calculated)** | 1.494 Mg/m$^3$ | 1.387 Mg/m$^3$ | 1.429 Mg/m$^3$ |
| **Absorption coefficient** | 10.321 mm$^{-1}$ | 1.485 mm$^{-1}$ | 1.610 mm$^{-1}$ |
| **F(000)** | 2256 | 1152 | 1168 |
| **Theta range for data collection** | 2.901 to 74.995°. | 4.113 to 74.991°. | 4.160 to 74.996°. |
| **Index ranges** | $-38 \leq h \leq 38$, $-12 \leq k \leq 11$, $-20 \leq l \leq 20$ | $-26 \leq h \leq 26$, $-13 \leq k \leq 10$, $-14 \leq l \leq 14$ | $-26 \leq h \leq 26$, $-13 \leq k \leq 13$, $-14 \leq l \leq 12$ |
| **Reflections collected** | 24717 | 16879 | 15299 |
| **Independent reflections** | 5106 [R(int) = 0.0405] | 5467 [R(int) = 0.0432] | 5370 [R(int) = 0.0365] |
| **Completeness to theta = 67.679°** | 99.8 % | 99.6 % | 99.9 % |
| **Absorption correction** | Semi-empirical from equivalents | Semi-empirical from equivalents | Semi-empirical from equivalents |
| **Max. and min. transmission** | 0.7539 and 0.6017 | 0.7539 and 0.6545 | 0.7539 and 0.6548 |
| **Refinement method** | Full-matrix least-squares on F$^2$ | Full-matrix least-squares on F$^2$ | Full-matrix least-squares on F$^2$ |
| **Data / restraints / parameters** | 5106 / 7 / 321 | 5467 / 0 / 353 | 5370 / 0 / 362 |
| **Goodness-of-fit on F$^2$** | 1.046 | 1.049 | 1.033 |
| **Final R indices [I>2sigma(I)]** | R1 = 0.0574, wR2 = 0.1646 | R1 = 0.0699, wR2 = 0.1963 | R1 = 0.0407, wR2 = 0.1052 |
| **R indices (all data)** | R1 = 0.0615, wR2 = 0.1711 | R1 = 0.0761, wR2 = 0.2029 | R1 = 0.0456, wR2 = 0.1120 |
| **Absolute structure parameter** | n/a | n/a | n/a |
| **Extinction coefficient** | n/a | n/a | n/a |
| **Largest diff. peak and hole** | 0.674 and -1.782 e.Å$^{-3}$ | 0.593 and -0.582 e.Å$^{-3}$ | 0.337 and -0.406 e.Å$^{-3}$ |
Figure S52. ORTEP drawing of (a) C0[OTf], (b) C1[OTf] and (c) C2[OTf] obtained by X-ray crystal analysis. Thermal ellipsoids are shown at 50% probability. H atoms have been omitted for clarity.
Mass spectrum (MS)

Mass spectrum (MS) were acquired on spectrometers at an ionization potential of 70 or 40 eV using electrospray ionization (ESI) with ion trap analyzers or fast atom bombardment (FAB) method. Peaks are listed according to their mass/charge (m/z) value with percent relative abundance. High-resolution mass spectrum (HRMS) were recorded in positive or negative mode on spectrometers using ESI equipped with time-of-flight (TOF) analyzers.

Figure S53. HRMS spectrum of compound C0[BPhCl].

Figure S54. HRMS spectrum of compound C1[BPhCl].
Figure S55. HRMS spectrum of compound C2[BPhCl].

Figure S56. LRMS (FAB-) spectrum of compound Z1Bs.

Chemical Formula: C27 H26 N2 O3 S
Exact Mass: 458.1664
**Figure S57.** LRMS (FAB+) spectrum of compound Z1Bs.

**Figure S58.** LRMS (FAB-) spectrum of compound Z2Bs.
Figure S59. LRMS (FAB+) spectrum of compound Z2Bs.
Photophysical properties

**Steady-state spectroscopy.** The UV-Vis absorption spectra and the emission spectra were performed by a U-3310 spectrophotometer (Hitachi) and a FLS980 fluorometer (Edinburgh Instrument), respectively. The calibration of the excitation and emission wavelength of FLS 980 were carefully done. The samples were prepared in a 1-cm length cuvette with the absorbance of 0.1 at the excitation wavelength.

**Time-resolved fluorescence spectroscopy.** The subnanosecond time-resolved measurement was carried out by a time-correlated single photon counting (TCSPC) system (OB-900, Edinburgh Instrument). One of the excitation light source was set up by second harmonic generation (SHG) of a pulse-selected tsunami femtosecond laser pulses of 820 nm and generating 430 nm light. Another excitation light source was set up by the third harmonic generation (THG) of 900 nm light generated from the same femtosecond laser and giving 300 nm light source. The fluorescence of the sample was collected at an angle of 90° with respect to the pump beam. A polarizer which is set at 54.7° with respect to polarization of pump beam was located on the light path of the pump beam in front of the detector to eliminate the anisotropy. The temporal resolution was estimated to be 15 ps after removing the instrument broadening. The ultrafast time-resolved spectroscopic studies were recorded by a FOG100 femtosecond up-conversion system (CDP) pumped by SHG of the same femtosecond pulse laser. In the experiment, the sample emission generated from a rotating sample cell and the interrogation gate pulse at designated delay time were focused on a BBO crystal with respect to the pump pulse for frequency summation. A λ/2 plate was used to set polarization at magic angle of 54.7° between pump and gate pulse to avoid fluorescence anisotropy. The femtosecond time-resolved data were fitted to the sum of exponential functions convoluted with the IRF, which is fitted to 150 fs determined by Raman scattering signal.

**Computational Methodology.** All the computational results were performed by the Gaussian 09 program. The ground-state (S₀) and first excited-state (S₁) geometry optimization for these pyridinium in toluene in combination with a polarizable continuum solvation model (PCM) were performed by density functional theory (DFT) and time-dependent density functional theory (TD-DFT) under 6-31+G(d,p) basis set, respectively. M062X hybrid function was used in this study. The absorption energies are calculated by the linear response approach under the corresponding ground state geometries.

**Measurement of Quantum Yield (Q.Y.)**

The method to measure Quantum yield is based on a previous report, the measurement is carried out by U3310 spectrophotometer and FLS980 fluorometer, then two dilute solution are prepared, one is the sample solution and the other one is the standard solution whose Q.Y. is already known. The Q.Y. can be calculated by the following equation:

\[
Q_f = \frac{F^i OD_s n_i^2}{F^s OD_t n_s^2} \left( \frac{Q^s}{Q^f} \right)
\]

Where \(Q_f^i\) and \(Q_f^s\) are the fluorescence Q.Y. of the sample and the standard, respectively; and the \(OD_s\) and \(OD_t\) are the absorbance of the solution of the sample and the standard at the same excitation wavelength, respectively; \(n_i\) and \(n_s\) presented the refractive indices of the sample and the standard solution.

For Z1Bs and t-Z2Bs, due to their poor solubility, photoluminescence Q.Y. for both compounds are estimated using the radiative rate constants of C1[OTf] and t-C2[OTf], which can be calculated from absorption spectra.
Table S4. The photophysical data of N0-1 in toluene, dichloromethane, acetonitrile at 298K.

| solvent | \(\lambda_{\text{abs}}\)/nm | \(\lambda_{\text{em}}\)/nm | Q.Y./% | \(\tau\)/ns |
|---------|-----------------|-----------------|--------|-------------|
| N0      |                 |                 |        |             |
| Tol     | 291             | 373             | 9      | 1.2         |
| DCM     | 292             | 404             | 12     | 3           |
| ACN     | 290             | 414             | 12     | 3.9         |
| N1      |                 |                 |        |             |
| Tol     | 345             | 409             | 57     | 2           |
| DCM     | 347             | 450             | 100    | 4.3         |
| ACN     | 342             | 480             | 60     | 5           |
| N2      |                 |                 |        |             |
| Tol     | 351             | 421             | 92     | 1.7         |
| DCM     | 353             | 475             | 76     | 2.7         |
| ACN     | 346             | 503             | 58     | 3.4         |

Table S5. The computed wavelength (\(\lambda\)), oscillator strength (\(f\)) and orbital transition assignments for compounds N0-2 at M062X/6-31+G(d,p) level.

| Transition | Wavelength (nm) | \(f\) | Assignments | Weight |
|------------|-----------------|-------|-------------|--------|
| N0         |                 |       |             |        |
| \(S_0\rightarrow S_1\) | 270.08       | 0.441 | HOMO\(\rightarrow\)LUMO | 95%    |
| \(S_0\rightarrow S_2\) | 267.66       | 0.1731| HOMO\(\rightarrow\)LUMO-1 | 92%    |
| \(S_1\rightarrow S_0\) | 320.66       | 0.2336| HOMO\(\rightarrow\)LUMO | 96%    |
| N1         |                 |       |             |        |
| \(S_0\rightarrow S_1\) | 309.21       | 0.8571| HOMO\(\rightarrow\)LUMO | 88%    |
| \(S_0\rightarrow S_2\) | 281.72       | 0.06  | HOMO\(\rightarrow\)LUMO+1 | 88%    |
| \(S_1\rightarrow S_0\) | 365.73       | 0.8291| HOMO\(\rightarrow\)LUMO | 94%    |
| N2         |                 |       |             |        |
| \(S_0\rightarrow S_1\) | 315.08       | 1     | HOMO\(\rightarrow\)LUMO | 73%    |
| \(S_0\rightarrow S_2\) | 281.8        | 0.0362| HOMO\(\rightarrow\)LUMO+1 | 87%    |
| \(S_1\rightarrow S_0\) | 388.14       | 1     | HOMO\(\rightarrow\)LUMO | 89%    |

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Figure S60. The frontier orbitals of (a) N0, (b) N1 and (c) N2 involved in first excited-state transition calculated by TD-DFT under m062x/6-31+g(d,p) level.

Table S6. The computed wavelength ($\lambda$), oscillator strength (f) and orbital transition assignments for compounds C0-2* at M062X/6-31+G(d,p) level.

| Compound | Transition | Wavelength (nm) | f       | Assignments          | Weight |
|----------|------------|-----------------|---------|-----------------------|--------|
| C0*      | $S_0\rightarrow S_1$ | 426.31          | 0.6326  | HOMO$\rightarrow$LUMO | 94%    |
|          | $S_0\rightarrow S_2$ | 271              | 0.0073  | HOMO$\rightarrow$LUMO+1 | 90%    |
|          | $S_1\rightarrow S_0$ | 633.04          | 0.0202  | HOMO$\rightarrow$LUMO | 96%    |
| C1*      | $S_0\rightarrow S_1$ | 426.31          | 1       | HOMO$\rightarrow$LUMO | 93%    |
|          | $S_0\rightarrow S_2$ | 308.34          | 0.0017  | HOMO$\rightarrow$LUMO+1 | 93%    |
|          | $S_1\rightarrow S_0$ | 537.31          | 0.5408  | HOMO$\rightarrow$LUMO | 94%    |
| C2*      | $S_0\rightarrow S_1$ | 464.74          | 0.7043  | HOMO$\rightarrow$LUMO | 91%    |
|          | $S_0\rightarrow S_2$ | 313.28          | 0.7668  | HOMO$\rightarrow$LUMO | 8%     |
|          | $S_1\rightarrow S_0$ | 534.29          | 1       | HOMO$\rightarrow$LUMO | 91%    |
Figure S61. The frontier orbitals of (a) C0+, (b) C1+ and (c) C2+ calculated involved in first excited-state transition by TD-DFT under m062x/6-31+g(d,p) level.

Figure S62. The excitation spectra of (a) C0[BPhCl], (b) C1[BPhCl] and (c) C2[BPhCl] in toluene at 298K.

Figure S63. The absorption (black line) and emission (red line) spectra for A. (a) C0[BPhCl], (b) C1[BPhCl] and (c) C2[BPhCl] in solid state at 298 K.
Figure S64. Kinetics trace by TCSPC for (a) C1[BPhCl] and (b) C2[BPhCl] in toluene at 298K. The instrument response function is shown in green line. \( \lambda_{\text{ex}}: 420 \text{ nm} \).

Table S7. Time-resolved data for C1[PFS/OTf] and C2[PFS/OTf] in toluene at 298K.

|        | \( \lambda_{\text{mon}} \) (nm) | \( \tau_{\text{obs}} \) [ps, (pre-factor)] |
|--------|-------------------------------|-----------------------------------------------|
| C1[PFS] | 550                           | 45                                             |
|        | 700                           | 40 (-0.07), 184 (184)                          |
| C1[OTf] | 550                           | 60                                             |
|        | 700                           | 56 (-0.11), 225 (0.89)                         |
| C2[PFS] | 560                           | 86                                             |
|        | 720                           | 60 (-0.23), 131 (0.77)                         |
| C2[OTf] | 560                           | 94                                             |
|        | 720                           | 83 (-0.18), 138 (0.82)                         |

Figure S65. Kinetics trace by TCSPC for (a) C2[PFS] and (b) C2[OTf] in toluene at 298K. The instrument response function is shown in green line. \( \lambda_{\text{ex}}: 420 \text{ nm} \).
Figure S66. Kinetics trace by TCSPC for (a) C1[PF6] and (b) C1[OTf] in toluene at 298K. The instrument response function is shown in green line. \( \lambda_{\text{ex}} \): 420 nm.

Figure S67. The early-stage kinetic traces for (a) C1[BPhCl] and (b) C2[BPhCl] acquired by fluorescence up-conversion measurements in acetonitrile at 298K. The blue line represents the instrument response function. \( \lambda_{\text{ex}} \): 430 nm.

Figure S68. The emission spectra of C2[OTf] in toluene at 298K. The green and red dashed lines are the deconvoluted bands.
Table S8. Photophysical data for Z1Bs, t-Z2Bs and t-C2[OTf] in toluene at 298K.

|          | PLQY\(^a\) | \(\tau_{\text{obs}}\) (ns) |
|----------|-------------|-----------------------------|
| Z1Bs     | 0.52        | 4                           |
| t-Z2Bs   | 0.67        | 3.3                         |
| t-C2[OTf]| 0.034       | 0.13                        |

\(^a\)Due to the low solubility, the photoluminescence quantum yields (PLQY) are estimated by \(k_r\) of C1[OTf] and t-C2[OTf], respectively.

**Figure S69.** Kinetics trace by TCSPC for (a) Z1Bs, (b) t-Z2Bs (c) t-C2[OTf] in toluene at 298K. \(\lambda_{\text{ex}}\): 420 nm.

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