Supporting Information

An AIE active monoimidazolium skeleton: high selectivity and fluorescence turn-on for $H_2PO_4^-$ in acetonitrile and ClO_4^- in water

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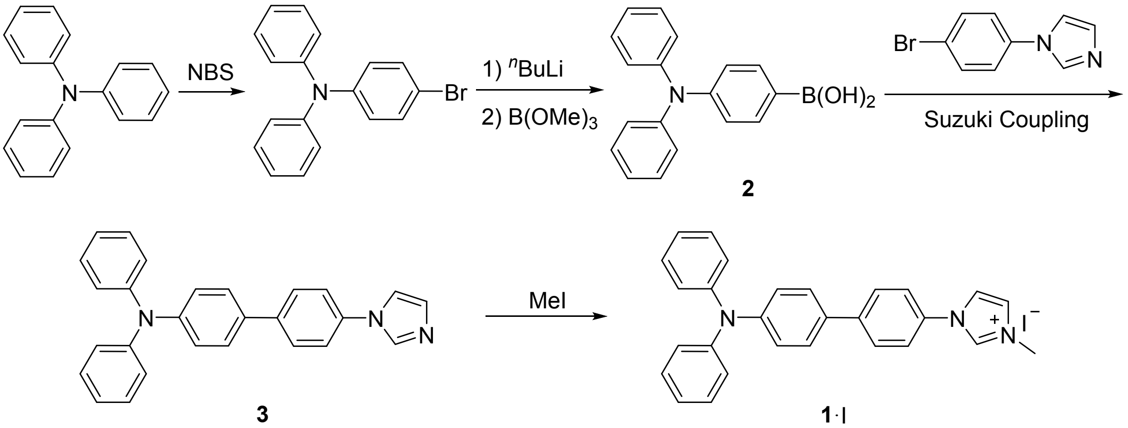
Table of Contents

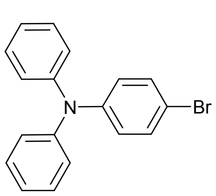
I. General remarks.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF) and toulene were heated under reflux with sodium and benzophenone, then distilled prior to use. Double-distilled water was used in the experiments. 1-(4-Bromo-phenyl)-1*H*-imidazole was synthesized according to the published procedures.[1]

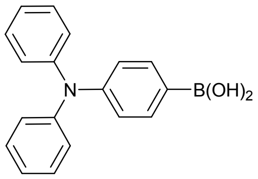
NMR spectra were obtained on a Bruker AV II-400 MHz spectrometer. The ^{1}H NMR (400 MHz) chemical shifts were measured relative to $CDCl_3$ as the internal reference ($CDCl_3$: δ = 7.26 ppm). The ^{13}C NMR (100 MHz) chemical shifts were given using $CDCl_3$ as the internal standard ($CDCl_3$: δ = 77.16 ppm). High-resolution mass spectra (HRMS) were obtained with a Waters-Q-TOF Premier (ESI). Melting points were determined with XRC-1 instrument and are uncorrected. Absorption spectrum was obtained on a HITACHI U-2910 spectrophotometer. Fluorescence spectra were collected on a Horiba Jobin Yvon-Edison Fluoromax-4 fluorescence spectrometer. Fluorescence microscopy images were taken on an OLYMPUS IX71 fluorescence microscope. Dynamic light scattering (DLS) experiments were carried out with ZEN3600 Malvern mastersizer, and the samples were filtered through the millipore filter prior to the experiments.

II. Synthesis of compound 1·I.

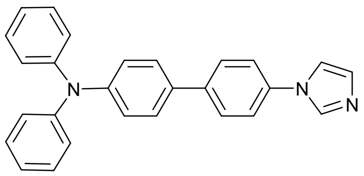




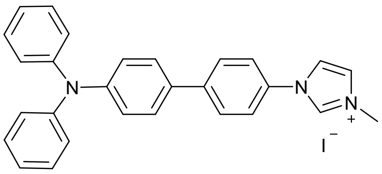
4-Bromo-*N*,*N*-diphenylaniline.[2] A mixture of triphenylamine (7.35 g, 30.0 mmol) and NBS (5.90 g, 33.0 mmol) in CCl_4 (125 mL) was refluxed for 10 h. The precipitates (succinimide) were filtered, and the filtrate was concentrated using rotavapor. The remaining gray oil was dispersed in ethanol, and the desired product was collected by filtration as a white solid (6.84 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.94 (d, J = 8.8 Hz, 2H), 7.01-7.09 (m, 6H), 7.25 (t, J = 7.8 Hz, 4H), 7.32 (d, J = 8.4 Hz, 2H) ppm.



4-(Diphenylamino)phenylboronic acid.[3] *n*-Butyllithium (6.4 mL, 2.5 M in hexane) was slowly added to a solution of 4-bromo-*N,N*-diphenylaniline (4.54 g, 14.0 mmol) in dry THF (42 mL) under N_2 at -78 ºC. The resulting solution was stirred for 1.5 h, and $B(OMe)_3$ (4.8 mL, 42.0 mmol) was then added. After stirring for another 45 min at -78 ºC, the mixture was allowed to stir at room temperature overnight. The reaction was quenched with 1 M HCl and extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$, filtered and concentrated using rotavapor. The residue was passed through a silica gel column (CH_2Cl_2/EtOAc = 10/1, v/v) to give **2** as a white solid (2.11 g, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.08-7.11 (m, 4H), 7.17 (d, J = 7.6 Hz, 4H), 7.30 (t, J = 7.8 Hz, 4H), 8.02 (d, J = 8.4 Hz, 2H) ppm.



4-(Diphenylamino)-4'-(imidazole-1-yl)-1,1'-biphenyl 3. A mixture of 4-(diphenylamino)phenylboronic acid (0.33 g, 1.5 mmol), 1-(4-bromo-phenyl)-1*H*-imidazole (0.43 g, 1.5 mmol), Pd(dppf)Cl_2 (0.066 g, 0.09 mmol), $BnEt_3NCl$ (0.021 g, 0.09 mmol) and CsF (0.68 g, 4.5 mmol) in toluene/H_2O (1:1, 4 mL) was refluxed overnight under N_2. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic phase was concentrated using rotavapor, and the residue was passed through a silica gel column (PE/Acetone = 2/1, v/v) to provide **3** as a white solid (0.43 g, 74% yield). M.p.: 152-154 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.06 (t, J = 7.4 Hz, 2H), 7.14-7.16 (m, 6H), 7.23 (s, 1H), 7.27-7.32 (m, 5H), 7.43-7.49 (m, 4H), 7.67 (d, J = 8.8 Hz, 2H), 7.90 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 118.3, 121.8, 123.3, 123.7, 124.7, 127.7, 128.0, 129.4, 130.5, 133.3, 135.6, 136.1, 140.1, 147.6, 147.8 ppm. HRMS (ESI$^+$): calcd for $C_{27}H_{22}N_3$ $[M+H]^+$ 388.1808, found 388.1814.



1-(4'-(Diphenylamino)-[1,1'-biphenyl]-4-yl)-3-methylimidazolium iodide 1·I. A mixture of **3** (0.39 g, 1.0 mmol) and iodomethane (0.3 mL, 5.0 mmol) in dry toluene (4 mL) was stirred under reflux for 4 h. The precipitates were filtered and purified by column chromatography on silica gel (CH_2Cl_2/MeOH = 50/1, v/v) to afford **1**·I as a white solid (0.38 g, 72% yield). M.p.: 220-223 ºC. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 4.28$ (s, 3H), 7.04-7.14 (m, 8H), 7.27-7.30 (m, 4H), 7.42 (d, $J = 8.4$ Hz, 2H), 7.67 (s, 2H), 7.71 (d, $J = 8.4$ Hz, 2H), 7.80 (d, $J = 8.4$ Hz, 2H), 10.46 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 37.8$, 120.6, 122.5, 123.3, 123.6, 124.4, 125.0, 127.9, 128.5, 129.6, 132.0, 132.8, 136.1, 143.2, 147.4, 148.5 ppm. HRMS (ESI$^+$): calcd for $C_{28}H_{24}N_3$ [M-I]$^+$ 402.1965, found 402.1962.

III. Fluorescence spectra of 1·I in CH_3CN/water mixture.

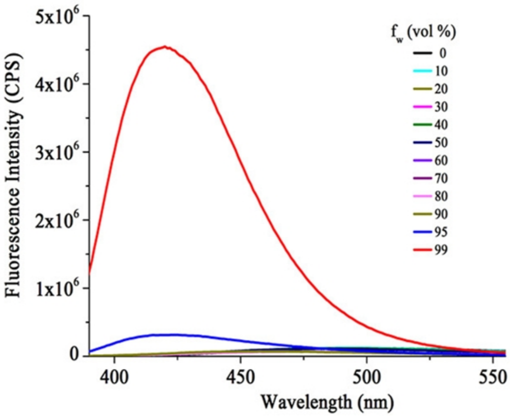


Fig. S1 The fluorescence spectra of **1**·I (10^{-4} M) in CH_3CN/water mixture with different fractions of water (f_w), excited at 376 nm, slit = 3 nm.

IV. Fluorescence spectra of **1**·I in the presence of other anions.

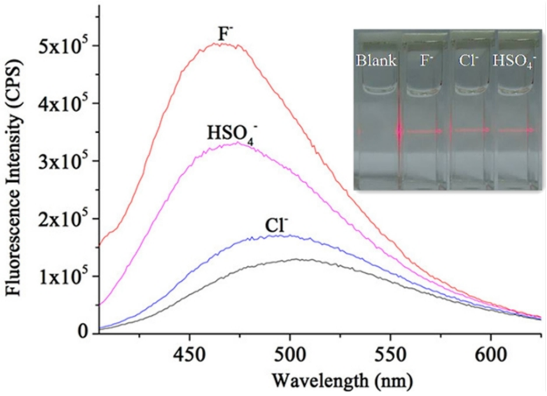


Fig. S2 The fluorescence spectra of **1**·I (5×10^{-4} M) in CH_3CN with TBAF, TBACl and $TBAHSO_4$ (10 equiv), respectively (excited at 392 nm, slit = 3 nm). Inset: The tyndall phenomenon of **1**·I (5×10^{-4} M) in the presence of different anions (10 equiv).

V. Job's Plot Measurement.

Stock solutions of **1**·I (10 μM) and $TBAH_2PO_4$ (10 μM) were prepared in CH_3CN, respectively. A total of 3 mL solutions of **1**·I and $TBAH_2PO_4$ in different volume ratios (**1**·I /anion: 3.0:0, 2.7:0.3, 2.4:0.6, 2.1:0.9, 2.0:1.0, 1.8:1.2, 1.5:1.5, 1.2:1.8, 0.9:2.1, 0.6:2.4, 0.3:2.7) were added to the quartz cells with well mixed. The spectra of the solutions were then recorded at room temperature. The difference in the fluorescence intensity at 462 nm was plotted against the mole fraction of $H_2PO_4^-$ at an invariant total concentration of 10 μM in CH_3CN.

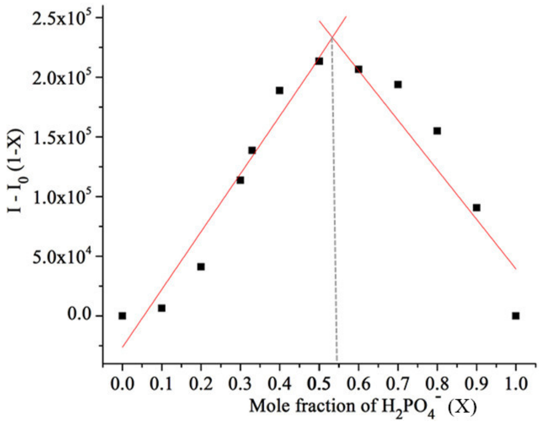


Fig. S3 Job's plot measured at 462 nm for determining the stoichiometry of **1**·I and $H_2PO_4^-$ ($X = [H_2PO_4^-]/([H_2PO_4^-] + [\mathbf{1}\cdot I])$, $[H_2PO_4^-] + [\mathbf{1}\cdot I] = 10$ μM) in CH_3CN.

VI. Fluorescence spectra of 1·H_2PO_4 and 1·I upon addition of $TBAH_2PO_4$.

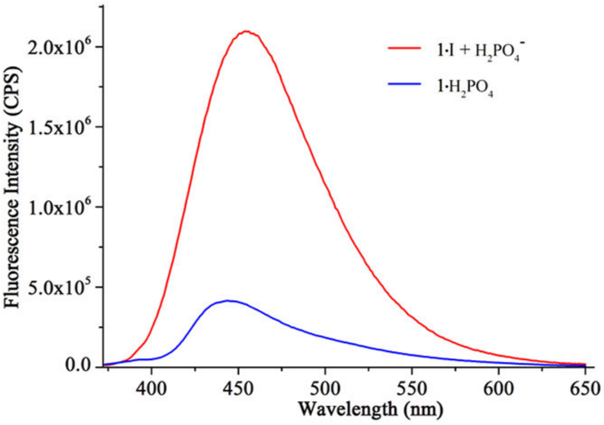


Fig. S4 The fluorescence spectra of **1**·H_2PO_4 (10 μM) and **1**·I (10 μM) in the presence of $H_2PO_4^-$ (10 equiv) in MeCN, respectively. Excited at 351 nm, slit = 3 nm.

VII. Fluorescence spectra of 1·H_2PO_4 in THF/HEPES mixture.

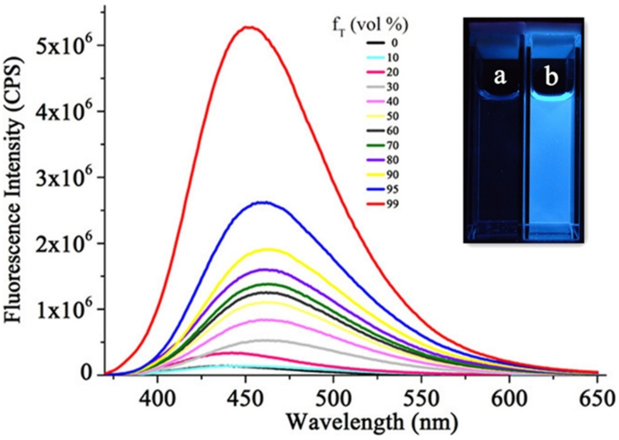


Fig. S5 The fluorescence spectra of **1**·H_2PO_4 (25 μM) in THF/HEPES mixture with different fractions of THF (f_T), excited at 355 nm, slit = 3 nm. Inset: The photos of **1**·H_2PO_4 in HEPES (a) and THF/HEPES mixture (b, 1/99, v/v) under UV light.

VIII. DLS profiles of 1 with H_2PO_4 and ClO_4 anions.

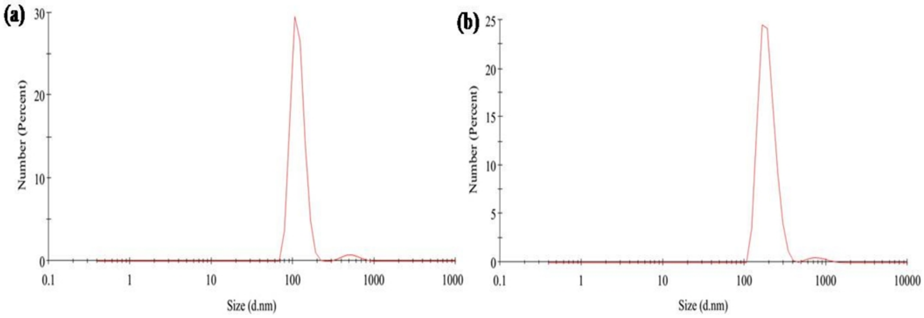


Fig. S6 (a) DLS profile of **1**·I (10 μM) in CH_3CN after the addition of $TBAH_2PO_4$ (10 equiv); (b) DLS profile of **1**·H_2PO_4 (25 μM) in HEPES (10 mM, pH = 7.4) after the addition of $LiClO_4 \cdot 3H_2O$ (15 equiv).

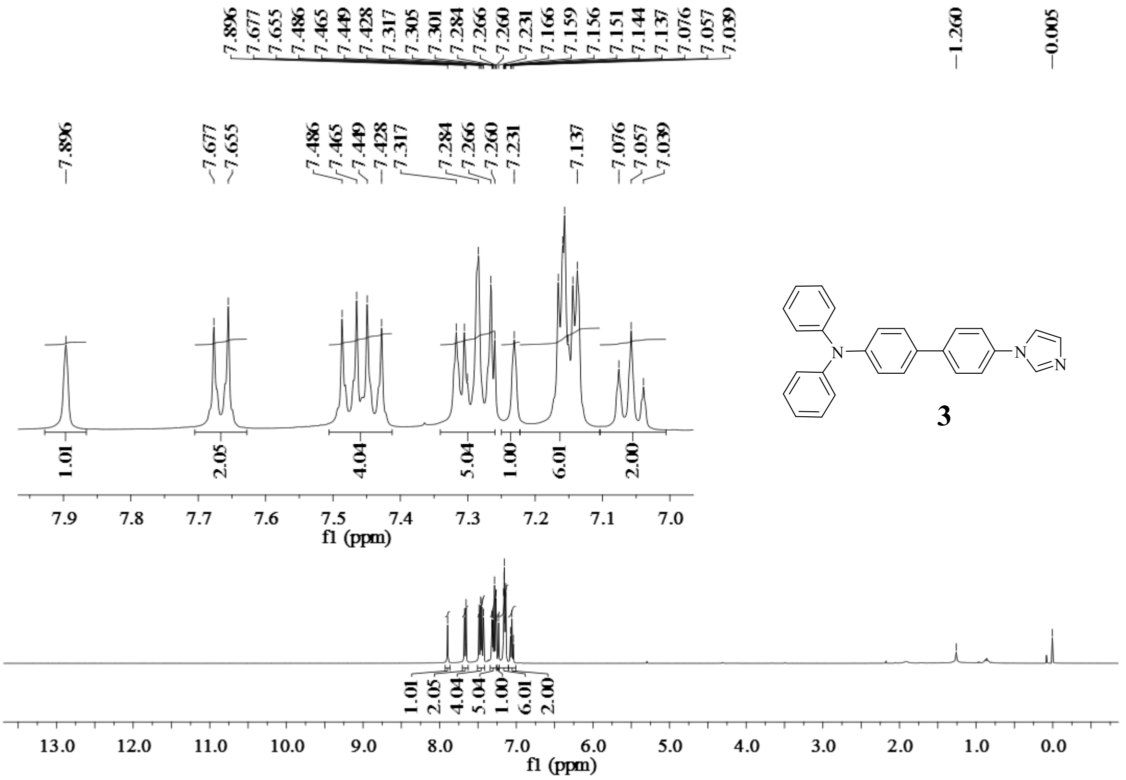
IX. References.

(1) L. Zhu, G. Li, L. Luo, P. Guo, J. Lan and J. You, *J. Org. Chem.*, 2009, **74**, 2200.

(2) H. Wang, G. Chen, Y. Liu, L. Hu, X. Xu and S. Ji, *Dyes and Pigments.*, 2009, **83**, 269.

(3) E. Guo, P. Ren, Y. Zhang, H. Zhang and W. Yang, *Chem. Commun.*, 2009, 5859.

X. Copies of ^{1}H NMR and ^{13}C NMR Spectra



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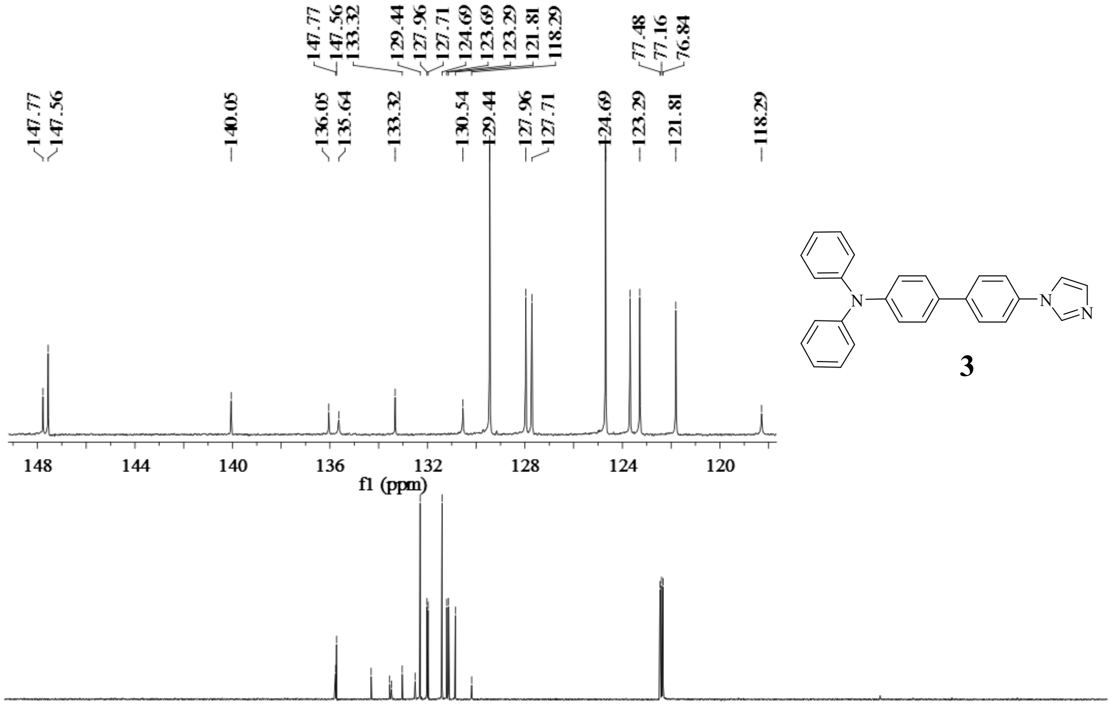

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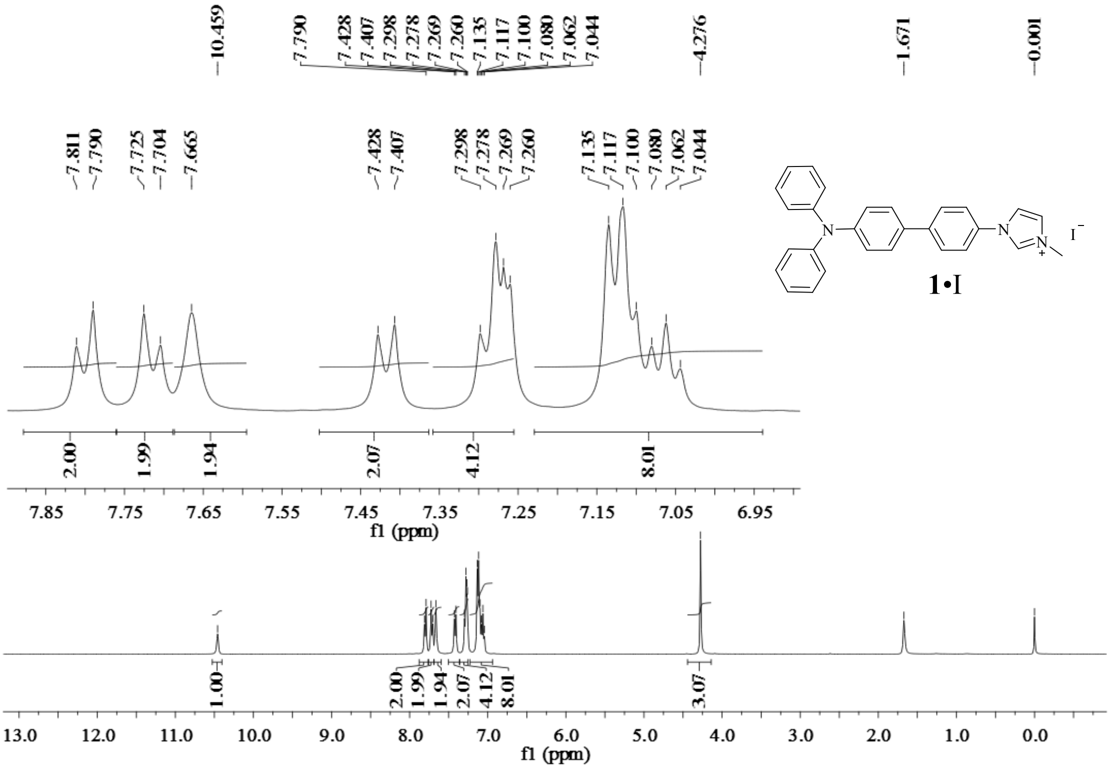
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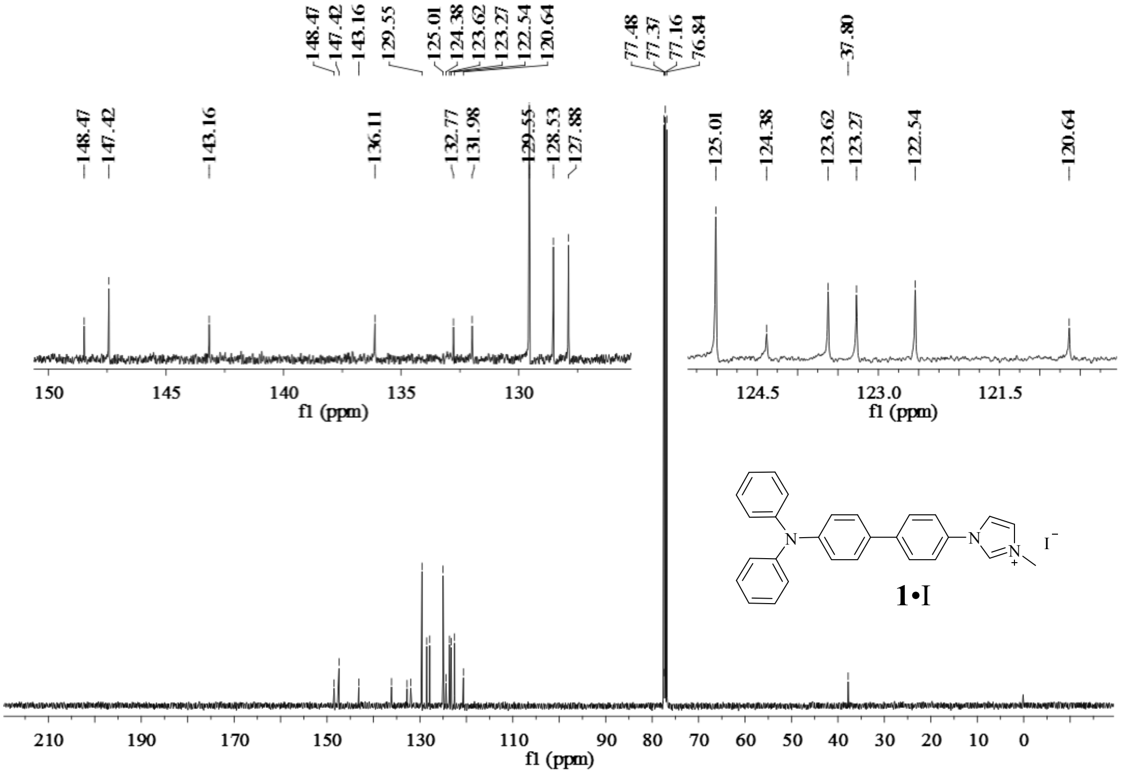
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