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Supporting information

Design of thermally activated delayed fluorescent sensitizers for high efficiency over 20% and long lifetime in the yellow fluorescent organic light-emitting diodes

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Experimental

General information

4-Bromobenzaldehyde, *N,N*-dimethylformamide and sodium tert-butoxide were purchased from Alfa Aesar of Themo Fisher Scientific Inc.. Pyridine, iodobenzene, piperidine were supplied from Sigma Aldrich Co.. Benzoylacetonitrile and benzimidamide were provided from J&H Chemical Co., LTD. Ethanol and tetrahydrofuran solvents were supplied from Samchun Pure Chemical Co.. 10,15-dihydro-5*H*-diindolo[3,2-*a*:3',2'-*c*]carbazole was supplied from Doosan Co.. Cesium carbonate (Cs_2CO_3), potassium carbonate (K_2CO_3) and potassium acetate (KOAc) were provided from Duksan Sci. Co.. 1,4-Dioxane and (3-cyano-4-fluorophenyl)boronic acid were provided from Daejung Chemicals & Metals CO. LTD. and LG Chem. Ltd. respectively. Tri-tert-butylphosphine, palladium(II) acetate, tetrakis(triphenylphosphine)palladium(0) and [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) were provided from P&H tech Co.. 2-Chloro-4,6-diphenyl-1,3,5-triazine was purchased from GOM Technology CO., LTD. All materials were used in the synthesis without further purification. General information about analysis was explained in our previous work.[24] High-performance liquid chromatography data of the final material purified after synthesis were attached in **Figure S7**. Gas chromatography high resolution mass spectrometry (GC-HRMS) was performed using a JEOL, JMS-700.

Synthesis

(*E*)-2-(4-bromobenzoyl)-3-phenylacrylonitrile (1)

Benzoylacetonitrile (10 g, 68.9 mmol) and 4-bromobenzaldehyde (14 g, 75.8 mmol) were dissolved in 150 mL of high purity ethanol in a 250 mL 2-neck round-bottomed (RB) flask. Piperidine (0.33 g, 3.86 mmol) was slowly dropped into the mixed solution. After mixing, the mixture was stirred and refluxed under a nitrogen atmosphere for 12 h. After the reaction was

completed, the temperature was lowered to room temperature and filtration was performed using n-hexane and ethanol. Filtered solid powder was recrystallized from ethanol and yellow powder (10.5 g) was obtained

Yield 45%, ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (s, 1H), 8.03 (d, J = 7.5 Hz, 2H), 7.90 (d, J = 8.5 Hz, 2H), 7.64 (t, J = 7.25 Hz, 1H), 7.58 (t, J = 7.25 Hz, 1H), 7.54-7.52 (m, 4H). MS (APCI) m/z [$(M+H)^+$] 234.09.

4-(4-Bromophenyl)-2,6-diphenylpyrimidine-5-carbonitrile (2)

(*E*)-2-(4-bromobenzoyl)-3-phenylacrylonitrile (10 g, 32.0 mmol) and benzamidine (5.77 g, 48.1 mmol) were dissolved in 150 mL of pyridine solvent, and the solution was stirred and refluxed under a nitrogen atmosphere for 18 h. After completion of the reaction, the mixture was filtered using hot ethanol. A yellowish white final product (3.1 g) was obtained without further purification.

Yield 27%, ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.66 (d, J = 7.0 Hz, 2H), 8.16 (d, J = 7.5 Hz, 2H), 8.06 (d, J = 8.5 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H), 7.62-7.75 (m, 6H). MS (APCI) m/z [$(M+H)^+$] 411.94.

5-(4,6-Diphenyl-1,3,5-triazin-2-yl)-2-fluorobenzonitrile (3)

2-Chloro-4,6-diphenyl-1,3,5-triazine (2 g, 7.47 mmol) and (3-cyano-4-fluorophenyl) boronic acid (1.47 g, 8.96 mmol) were completely dissolved in tetrahydrofuran (40 ml) under a nitrogen atmosphere. K_2CO_3 (3.10 g, 22.41 mmol) was dissolved in 20 mL distilled water (20 ml) and was added to the mixture. Tetrakis (triphenylphosphine) palladium (0) (0.26 g, 0.22 mmol) was added with stirring and refluxed for 12 h. When the reaction was completed, the temperature

was lowered to room temperature and then mixture was filtered. The filtered solid residue was washed three times with methylene chloride and a final product (2.20 g) was obtained.

Yield 84%, ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.08-9.06 (m, 1H), 9.03-3.01 (m, 1H), 8.74 (t, J = 8.5 Hz, 4H), 7.67-7.58 (m, 6H), 7.43-7.40 (m, 1H). MS (APCI) m/z [$(M+H)^+$] 353.43.

5,10-Diphenyl-10,15-dihydro-5*H*-diindolo[3,2-*a*:3',2'-c]carbazole (TruX)

10,15-Dihydro-5*H*-diindolo[3,2-*a*:3',2'-*c*]carbazole (10.0 g, 28.9 mmol), iodobenzene (11.6 g, 57.0 mmol) and sodium *tert*-butoxide (11.1 g, 115.8 mmol) were dissolved in 1,4-dioxane (250 ml). Palladium(II) acetate (0.26 g, 1.16 mmol) and tri-*tert*-butylphosphine (0.88 g, 4.30 mmol) were additionally put into the mixture under a nitrogen atmosphere. After stirring at 120 °C using oil bath for 18 h, the temperature of the mixture was lowered to room temperature, and the base and the catalyst were removed filtration. The collected filtrate was purified by column chromatography to obtain a white powder (6.82 g) using a mixed eluent of dichloromethane: n-hexane (1: 1). The white powder was not further purified because the mixture material was 5,10,15-triphenyl-10,15-dihydro-5*H*-diindolo [3,2-*a*: 3 ', 2'-*c*] carbazole linked by three phenyls.

Yield 47%, MS (APCI) m/z [$(M+H)^+$] 498.55.

4-(4-(10,15-Diphenyl-10,15-dihydro-5*H*-diindolo[3,2-*a*:3',2'-*c*]carbazol-5-yl)phenyl)-2,6-diphenylpyrimidine-5-carbonitrile (PyCNTruX)

4-(4-Bromophenyl)-2,6-diphenylpyrimidine-5-carbonitrile (0.8 g, 1.94 mmol), 5,10-diphenyl-10,15-dihydro-5*H*-diindolo[3,2-*a*:3',2'-c]carbazole (1.06 g, 2.13 mmol) and sodium *tert*-butoxide (0.37 g, 3.88 mmol) were dissolved in toluene (100 ml). Tris(dibenzylideneacetone)dipalladium(0) (0.05 g, 0.06 mmol) and tri-*tert*-butylphosphine (0.12 g, 0.58 mmol) were further added to the mixture under a nitrogen atmosphere. After

stirring and reflux for 1 h, the temperature of the mixture was lowered to room temperature and the base and the catalyst were removed by filtration. The collected filtrate was purified by column chromatography to obtain a yellowish orange powder (1.45 g) using a mixed eluent of dichloromethane : n-hexane (1 : 1). To improve the purity of the final compound obtained by column chromatography, sublimation purification was carried out to obtain a highly pure product (1.03 g).

Yield 64%, ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.63 (d, J = 8.5 Hz, 2H), 8.44 (d, J = 8.5 Hz, 2H), 8.52-8.23 (m, 2H), 8.01 (d, J = 8.0 Hz, 2H), 7.73-7.63 (m, 16H), 7.46 (d, J = 8.5 Hz, 1H), 7.30-7.17 (m, 5H), 6.86-6.73 (m, 3H), 6.24 (d, J = 8.0 Hz, 1H), 6.02-5.99 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 102.15, 103.76, 104.00, 104.10, 109.93, 117.20, 120.05, 120.41, 121.60, 121.67, 121.83, 121.99, 122.05, 122.12, 123.59, 123.62, 123.75, 128.59, 128.68, 128.70, 128.75, 128.95, 129.06, 129.50, 130.27, 131.45, 131.65, 132.51, 135.81, 135.95, 136.78, 136.94, 137.07, 140.05, 140.90, 141.20, 142.74, 163.75, 168.73, 169.19. MS (APCI) m/z [$(M+H)^+$] 829.95. Gas chromatography high resolution mass spectrometry (m/z): [$(M+H)^+$] calculated for $C_{59}H_{36}N_6$, 829.3080; found, 829.3077.

5-(4,6-Diphenyl-1,3,5-triazin-2-yl)-2-(10,15-diphenyl-10,15-dihydro-5*H*-diindolo[3,2-*a*:3',2'-*c*]carbazol-5-yl)benzonitrile (TCNTruX)

5-(4,6-Diphenyl-1,3,5-triazin-2-yl)-2-fluorobenzonitrile (0.7 g, 1.99 mmol), 5,10-diphenyl-10,15-dihydro-5*H*-diindolo[3,2-*a*:3',2'-c]carbazole (1.09 g, 2.19 mmol) and cesium carbonate (1.94 g, 5.96 mmol) were dissolved in *N,N*-dimethylformamide (25 ml) in a 100 mL ace pressure tube. The lid of the ace pressure tube was sealed and then stirred at 190 °C in an oil bath for 6 h. After the reaction was completed, the temperature was lowered to room temperature and the mixture was extracted four times using distilled water and methylene chloride. The organic layer was dried over $MgSO_4$ and the final compound was purified by

column chromatography (dichloromethane: n-hexane = 1: 4). A yellow powder (1.35 g) obtained by column chromatography was purified by sublimation purification to obtain a highly pure compound (1.25 g).

Yield 76%, ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.62 (s, 1H), 9.29 (d, J = 8.0 Hz, 1H), 8.85 (d, J = 7.0 Hz, 4H), 8.09 (d, J = 8.0 Hz, 1H), 7.75-7.67 (m, 16H), 7.38 (d, J = 8.5 Hz, 1H), 7.32-7.22 (m, 4H), 7.18 (t, J = 8.0 Hz, 1H), 6.85-6.76 (m, 3H), 6.21 (d, J = 8.0 Hz, 1H), 6.03 (d, J = 8.0 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 103.83, 104.62, 104.66, 110.01, 110.21, 110.45, 113.19, 115.82, 120.19, 120.38, 121.12, 121.26, 121.49, 122.11, 122.27, 122.66, 123.94, 124.12, 128.55, 129.01, 129.04, 130.32, 130.90, 134.77, 135.01, 136.53, 136.69, 136.80, 137.21, 139.95, 140.46, 141.25, 141.41, 146.08, 168.88, 171.47. MS (APCI) m/z [(M+H)$^{+}$] 830.83. Gas chromatography high resolution mass spectrometry (m/z): [(M+H)$^{+}$] calculated for $C_{58}H_{36}N_7$, 830.3032; found, 830.3032.

Device fabrication and measurements

TADF devices were fabricated based on the same device structure of indium tin oxide indium tin oxide (ITO, 120 nm)/ *N*,*N*'-diphenyl-*N*,*N*'-bis-[4-(phenyl-m-tolyl-amino)-phenyl]-biphenyl-4,4'-diamine (DNTPD, 60 nm)/ *N,N,N'N'*-tetra[(1,10-biphenyl)-4-yl]-(1,10-biphenyl)-4,4'-diamine (BPBPA, 20 nm)/ 9,9-dimethyl-10-(9-phenyl-9*H*-carbazol-3-yl)-9,10-dihydroacridine) (PCZAC, 10 nm)/emitting layer (30 nm)/ 2,8-bis(4,6-diphenyl-1,3,5-triazin-2-yl)dibenzo[*b,d*]furan (DBFTrz, 5 nm)/ 2-(4-(9,10-di(naphthalen-2-yl)anthracen-2-yl)phenyl)-1-phenyl-1*H*-benzo[*d*]imidazole (ZADN, 30 nm)/LiF (1.5 nm)/Al (200 nm). The emitting layers were PyCNTruX and TCNTruX doped PBICT at 20wt% doping concentration in the TADF devices. They were TADF sensitizer and fluorescent dopant co-doped PBICT in the TADF sensitized fluorescent OLEDs. The doping concentrations of the TADF sensitizer and fluorescent dopant were 20 wt% and 0.5%, respectively. TBRb was the fluorescent dopants

for the yellow devices, respectively. All device fabrication processes were performed by vacuum thermal evaporation. Device performance measurements were performed using an encapsulated device under an ambient condition. Keithley 2400 and CS 1000 (Konica Minolta Inc.) were used for the measurement of electrical and optical characteristics. The lifetime data of all device were measured using Polaronix (McScience Co.) lifetime measurement system equipped with electrical source and photodiode.

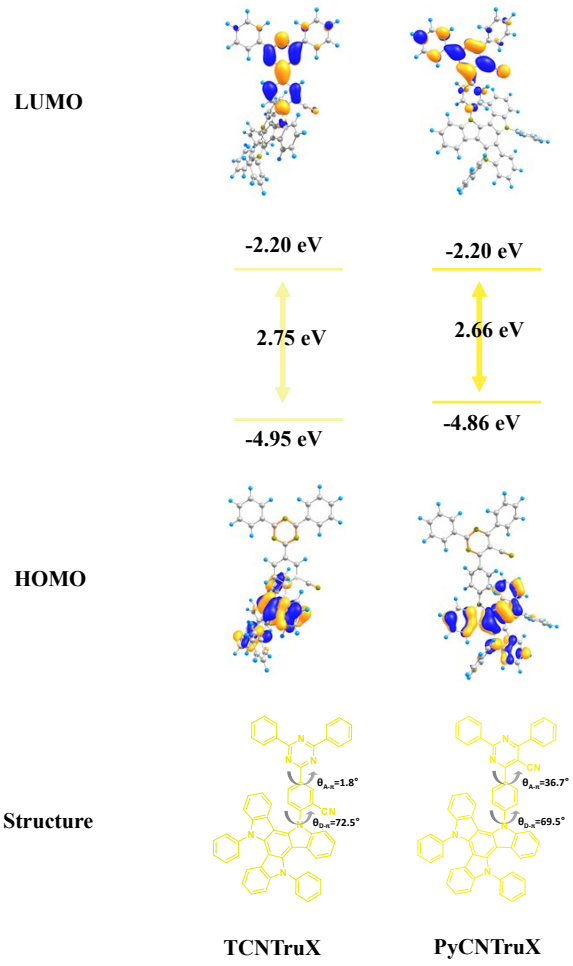

Figure S1. Simulated HOMO and LUMO distribution of TCNTruX and PyCNTruX.

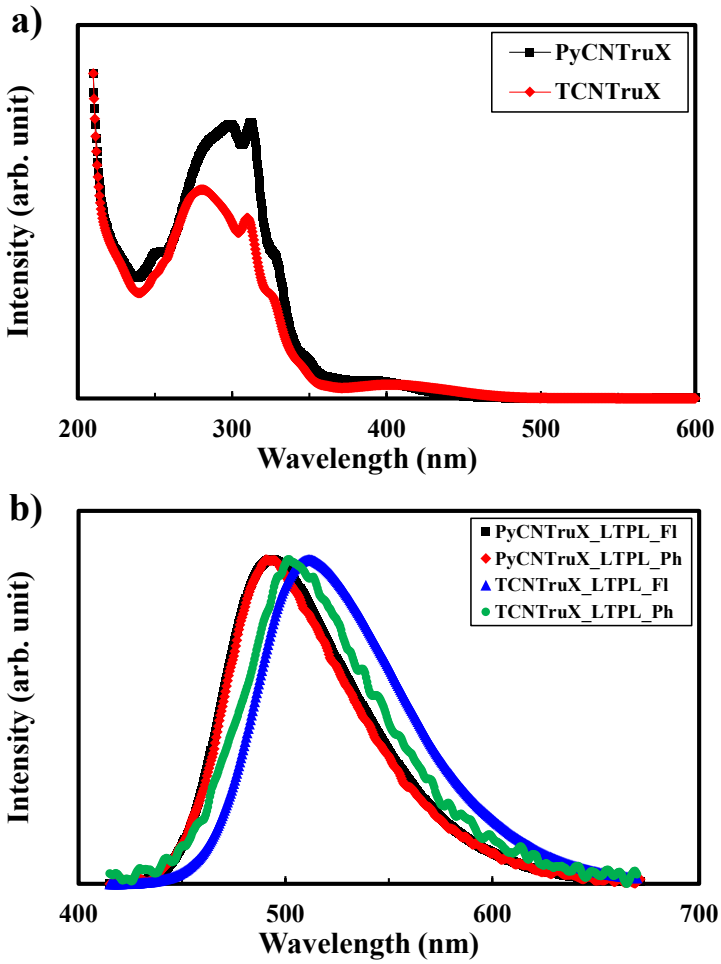

Figure S2. UV-vis (a) and low temperature PL of fluorescent and phosphorescent spectra (b) of PyCNTruX and TCNTruX.

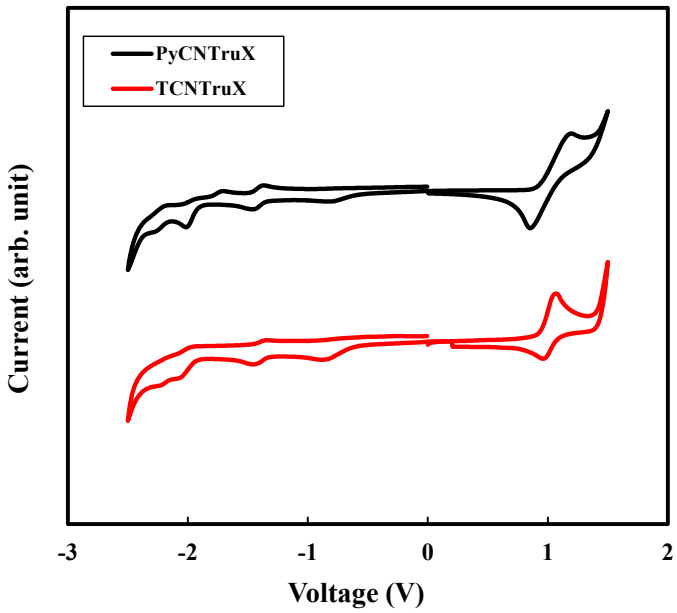

Figure S3. Cyclic voltammetry curves for the oxidation and reduction of PyCNTruX and TCNTruX.

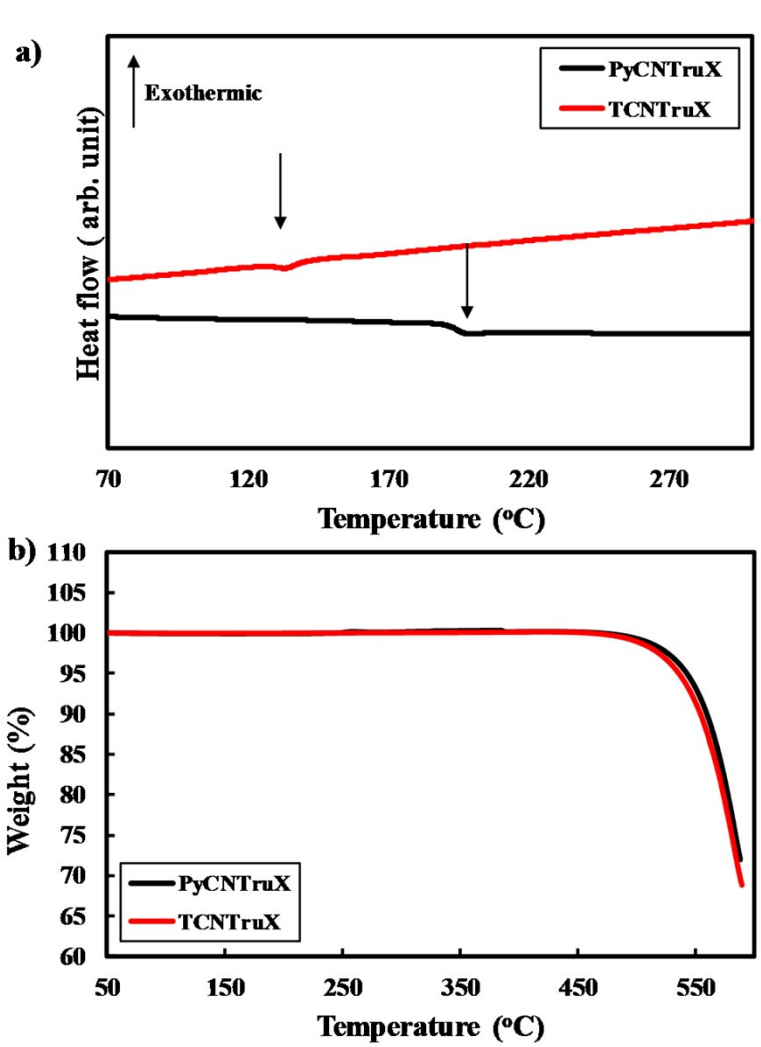

Figure S4. DSC a) and TGA b) thermograms of PyCNTruX and TCNTruX at a heating rete of 10 °C/min under a nitrogen atmosphere.

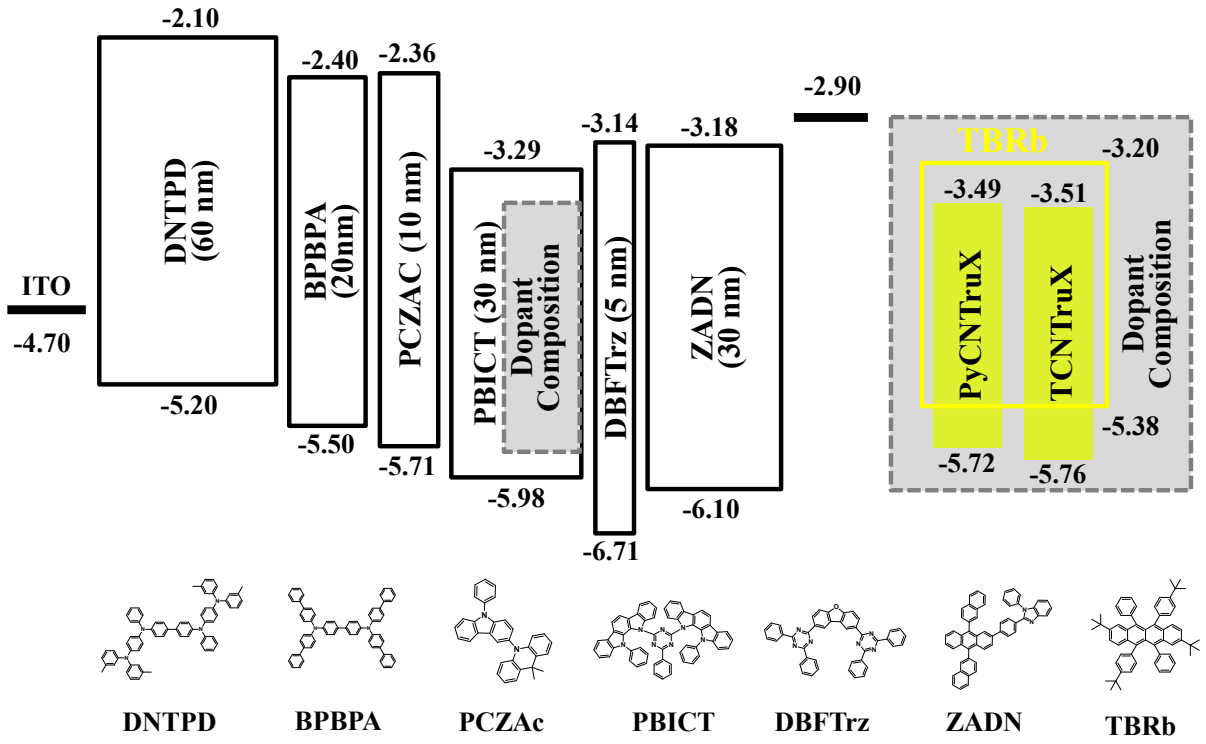

Figure S5. Energy level diagram of the PyCNTruX and TCNTruX in TADF and sensitized TBRb devices.

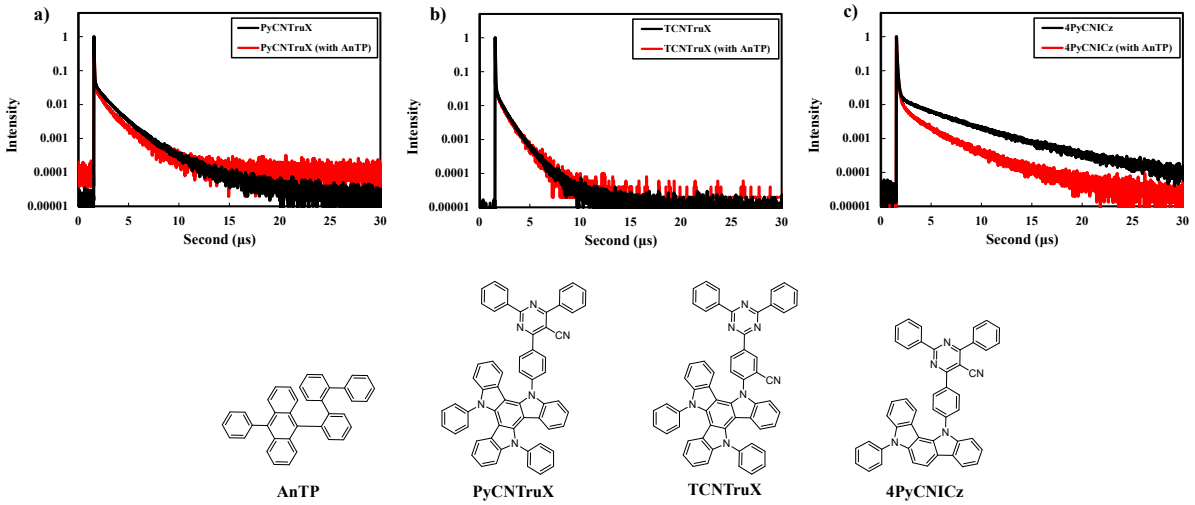

Figure S6. The transient PL decay curves of a) PBICT:PyCNTruX, b) PBICT:TCNTruX and c) PBICT:4PyCNICz films with or without AnTP doping.

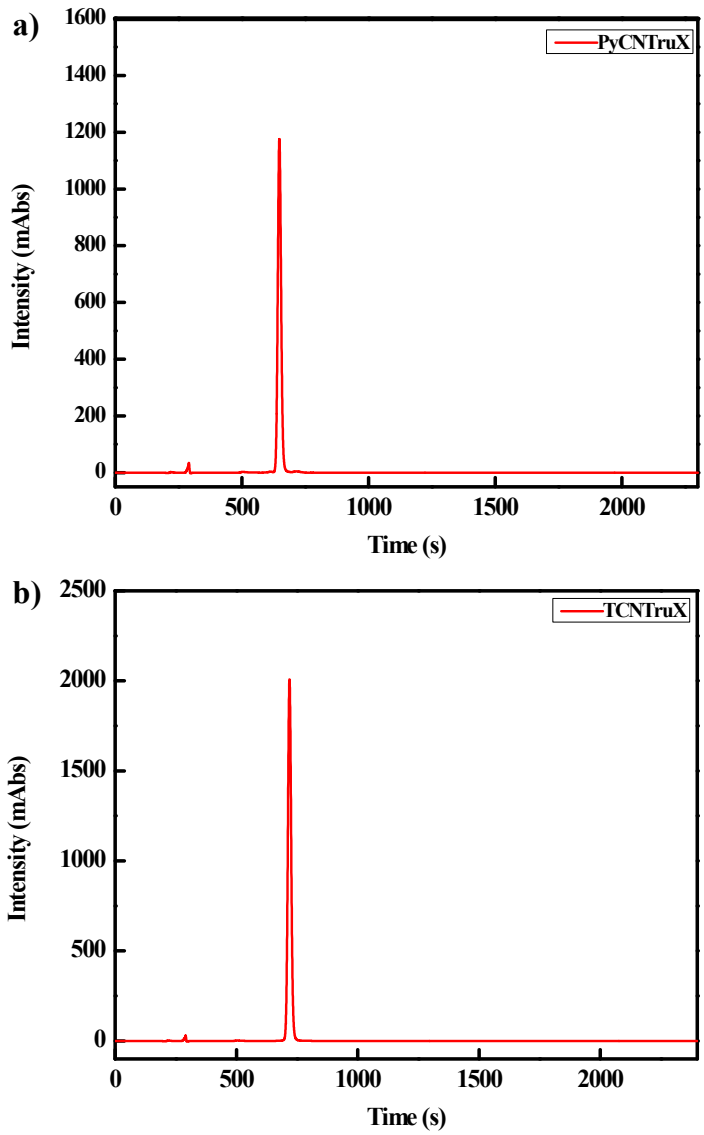

Figure S7. High-performance liquid chromatography (HPLC) data of a) PyCNTruX and b) TCNTruX.

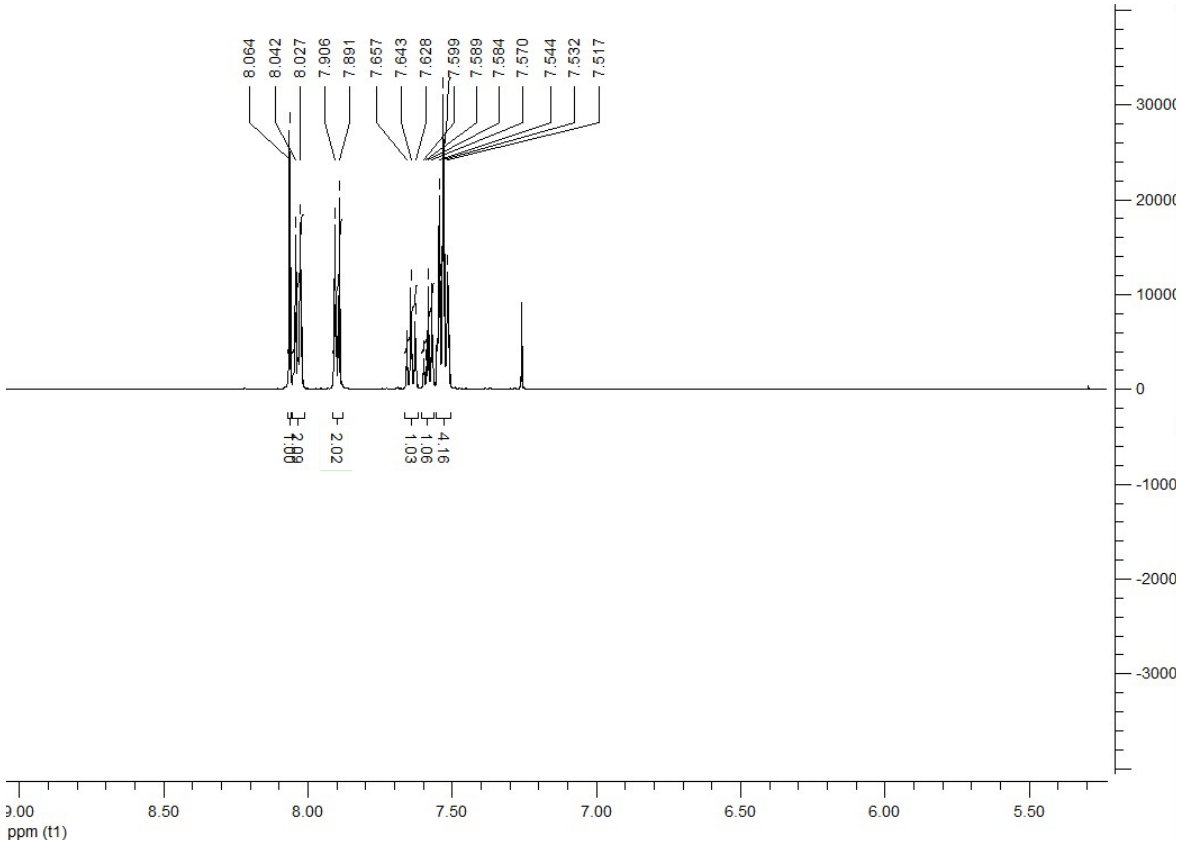

Figure S8. ^{1}H NMR spectrum of (*E*)-2-(4-bromobenzoyl)-3-phenylacrylonitrile in $CDCl_3$ at 25 °C

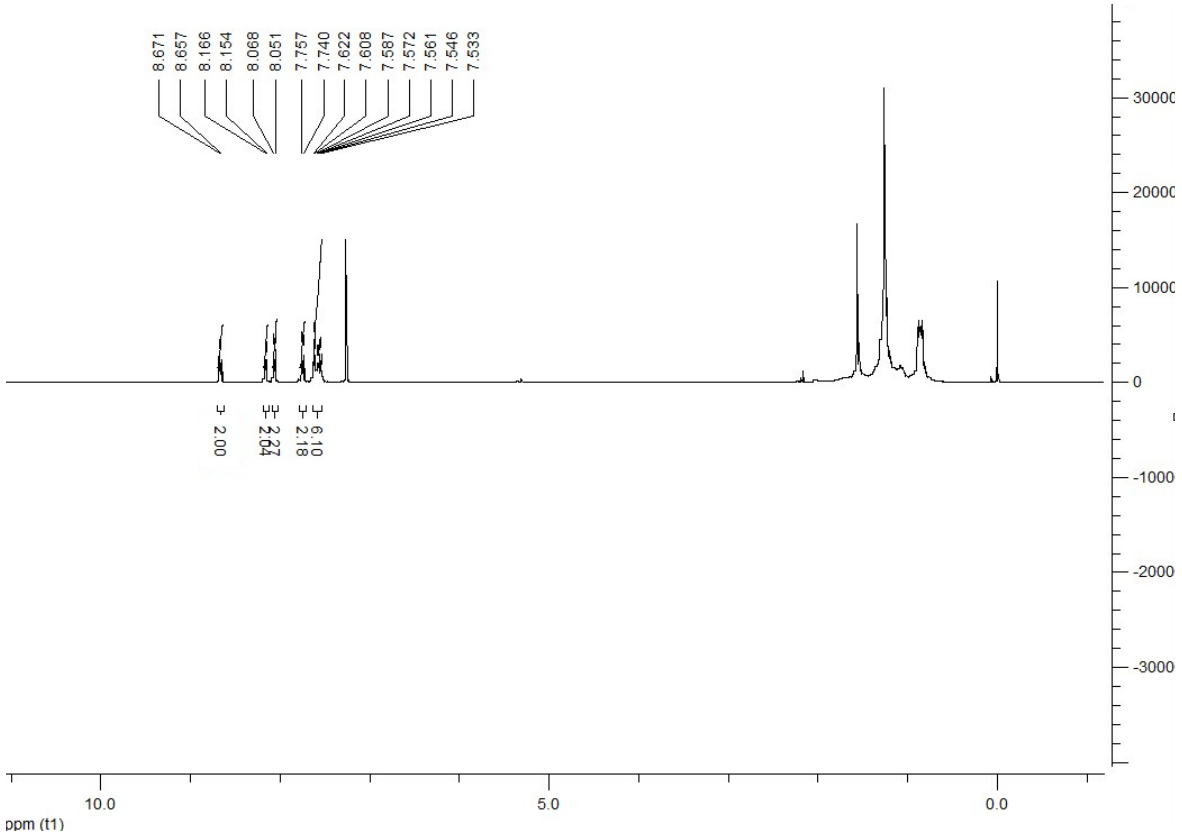

Figure S9. ^{1}H NMR spectrum of 4-(4-bromophenyl)-2,6-diphenylpyrimidine-5-carbonitrile in $CDCl_3$ at 25 °C

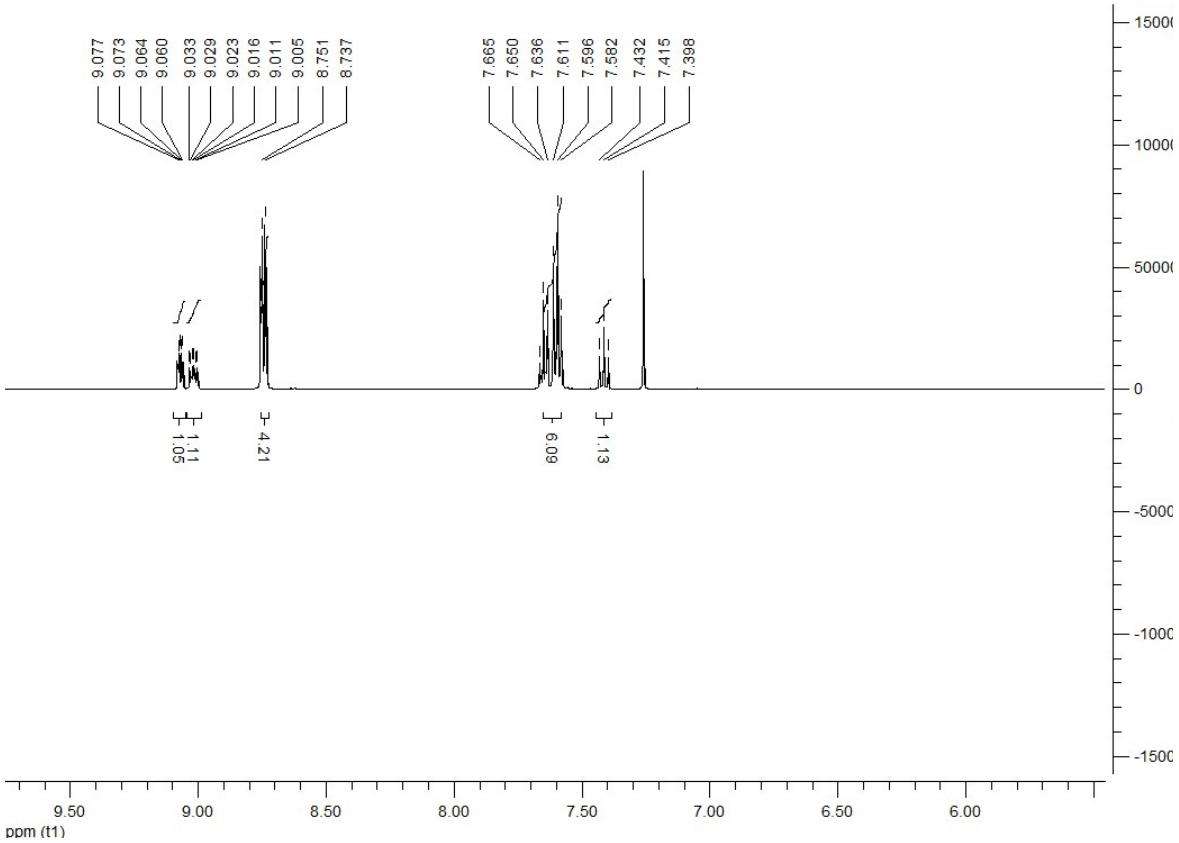

Figure S10. ^{1}H NMR spectrum of 5-(4,6-diphenyl-1,3,5-triazin-2-yl)-2-fluorobenzonitrile in $CDCl_3$ at 25 °C