Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

# Support Information

# Designing highly fluorescent, arylated poly(phenylene vinylene)s of intrinsic microporosity

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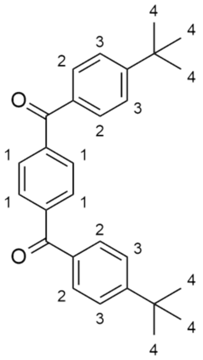
## Synthesis and structural characterization of model compounds and polymers

### 4,4‘-Bis(*tert*-butyl)terephthalophenone



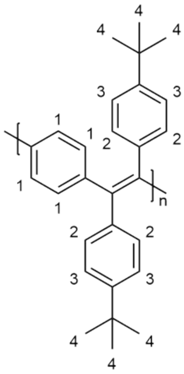
Terephthaloyl chloride (4.00 g, 19.70 mmol, 1.0 eq) was added to *tert*-butylbenzene (45.6 ml, 0.30 mol, 15.0 eq) and aluminium chloride (7.88 g, 59.10 mmol, 3.0 eq) in a dry flask under argon. The solution was stirred at room temperature for 1 hour. Subsequently, concentrated, aqueous hydrochloric acid (200 ml) was added. Then, the aqueous phase was separated and the organic layer was dried over sodium sulfate. The solvent was evaporated in vacuo and the crude product was purified by recrystallization from ethyl acetate to yield a white crystalline solid (2.50 g, 6.27 mmol, 32%).

**$^1$H-NMR** (400 MHz, $CDCl_3$, 300 K): δ [ppm] = 7.88 (s, 4H, $H_1$), 7.80 (d, $J$ = 8.4 Hz, 4H, $H_{2/3}$), 7.53 (d, $J$ = 8.4 Hz, 4H, $H_{2/3}$), 1.38 (s, 18H, $H_4$).

**$^{13}$C-NMR** (101 MHz, $CDCl_3$, 300 K): δ [ppm] = 195.9, 157.0, 141.0, 134.4, 130.4, 129.7, 125.6, 35.3, 31.3.

**MS** (APCI): m/z = 399.2347 calculated for $[C_{28}H_{31}O_2]^+$ = 399.2319.

**Poly[1,4-phenylene-1,2-bis(4-*tert*-butylphenyl)vinylene] (Poly-t-Bu)**



Chlorobenzene (45 ml) was added to 4,4’-bis(*tert*-butyl)terephthalophenone (1.81 g, 4.54 mmol, 1.0 eq) and phosphorus pentachloride (3.78 g, 18.16 mmol, 4.0 eq) in a Schlenk tube under argon atmosphere. The solution was stirred for 4 days at 120 °C. Subsequently, the solvent, phosphorus oxychloride and excess phosphorus pentachloride were removed by distillation under reduced pressure. The resulting 1,4-bis[dichloro(4-*tert*-butylphenyl)methyl]benzene was used without further purification.

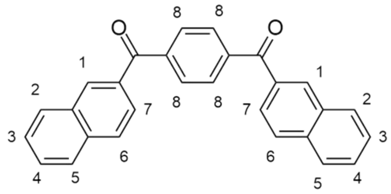
1,4-Bis[dichloro(4-*tert*-butylphenyl)methyl]benzene (2.31 g, 4.54 mmol, 1.0 eq) and dicobalt octacarbonyl (4.24 g, 12.40 mmol, 2.7 eq) where dissolved in chlorobenzene (10 ml) under argon atmosphere. The solution was heated to 100 °C for 50 minutes. Then, 1,2-dichloroethane (10 ml) was added and stirred for further 10 minutes. The polymer was precipitated by addition to acidified (2 M HCl) cold methanol, filtrated and washed with methanol. The crude product was purified by Soxhlet extraction (MeOH, acetone, EtOAc, $CHCl_3$). The ethyl acetate and chloroform fractions were re-precipitated by addition to acidified (2 M HCl) cold methanol. The product was obtained as a yellow solid (ethyl acetate fraction: 0.34 g, 0.92 mmol, 20%; chloroform fraction: 0.70 g, 1.90 mmol, 42%).

**$^1$H-NMR** (600 MHz, $C_2D_2Cl_4$, 353 K): $\delta$ [ppm] = 7.30-6.45 (m, 12H, $H_{1\text{-}3}$), 1.45-1.07 (m, 18H, $H_4$).

**$^{13}$C-NMR** (151 MHz, $C_2D_2Cl_4$, 353 K): $\delta$ [ppm] = 149.5, 144.5, 142.3, 141.0, 131.3, 131.0, 125.2, 124.5, 34.7, 31.8, 31.7.

**GPC** ($CHCl_3$): ethyl acetate fraction: $M_n$ = 9900 g/mol, $M_w$ = 3900 g/mol; chloroform fraction: $M_n$ = 29300 g/mol, $M_w$ = 164000 g/mol.

### 2,2'-Bis(naphthyl)terephthalophenone



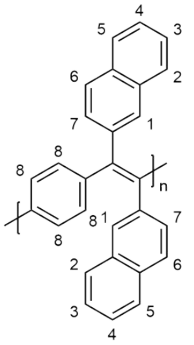
Terephthaloyl chloride (2.63 g, 12.95 mmol, 1.0 eq) was added to naphthalene (3.65 g, 28.48 mmol, 2.2 eq) and aluminium chloride (3.80 g, 28.50 mmol, 2.2 eq) in dichloroethane (130 ml) under argon at 0°C. The solution was stirred at room temperature for 20 hours. Subsequently, cold water was added. Then, the aqueous phase was separated and the organic layer was dried over magnesium sulfate. The solvent was evaporated in vacuo and the crude product was purified by column chromatography (hexane → DCM), The product was obtained as white solid (0.45 g, 1.16 mmol, 9%) yield.

**$^1$H-NMR** (600 MHz, $CDCl_3$, 300 K): δ [ppm] = 8.32 (s, 2H, $H_1$), 8.03-7.97 (m, 8H, $H_{2,5,8}$), 7.96-7.92 (m, 4H, $H_{6,7}$), 7.65 (t, *J*=7.4 Hz, 2H, $H_{3/4}$), 7.59 (t, *J* = 7.5 Hz, 2H, $H_{3/4}$).

**$^{13}$C-NMR** (151 MHz, $CDCl_3$, 300 K): δ [ppm] = 196.2, 141.2, 135.7, 134.4, 132.5, 132.4, 130.0, 129.7, 128.8, 128.7, 128.1, 127.2, 125.7.

**MS** (ESI): m/z = 409.1175 calculated for $[C_{28}H_{18}O_2Na]^+$ = 409.1199.

### Poly[1,4-phenylene-1,2-bis(2-naphthyl)vinylene] (Poly-Np1)



Chlorobenzene (10 ml) was added to 2,2'-bis(naphthyl)terephthalophenone (0.45 g, 1.16 mmol, 1.0 eq) and phosphorus pentachloride (0.97 g, 4.66 mmol, 4.0 eq) in a Schlenk tube under argon atmosphere. The solution was stirred for 24 hours at 120 °C. Subsequently, the solvent, phosphorus oxychloride and excess phosphorus pentachloride were removed by distillation under reduced pressure. The resulting 1,4-bis[dichloro(2-naphthyl)methyl]benzene was used without further purification.

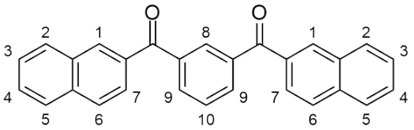
1,4-Bis[dichloro(2-naphthyl)methyl]benzene (0.58 g, 1.16 mmol, 1.0 eq) and dicobalt octacarbonyl (1.08 g, 3.17 mmol, 2.7 eq) where dissolved in chlorobenzene (10 ml) under argon atmosphere. The solution was heated to 100 °C for 50 minutes. Then, 1,2-dichloroethane (10 ml) was added and stirred for further 10 minutes. The Polymer was precipitated by addition to acidified (2 M HCl) cold methanol, filtrated and washed with methanol. The crude product was purified by Soxhlet extraction (MeOH, acetone, EtOAc, $CHCl_3$). The ethyl acetate and chloroform fractions were re-precipitated by addition to acidified (2 M HCl) cold methanol. The product was obtained as an orange solid (ethyl acetate fraction: 0.08 g, 0.23 mmol, 20%; chloroform fraction: 0.29 g, 0.81 mmol, 69%).

**$^1$H-NMR** (600 MHz, $C_2D_2Cl_4$, 353 K): δ [ppm] = 7.82-6.45 (m, 18H, $H_{1-8}$).

**$^{13}$C-NMR** (151 MHz, $C_2D_2Cl_4$, 353 K): δ [ppm] = 142.6, 141.5, 133.6, 132.6, 131.5, 131.0, 129.8, 128.5, 127.9, 127.2, 126.1.

**GPC** (THF): ethyl acetate fraction: $M_n$ = 4500 g/mol, $M_w$ = 6000 g/mol; chloroform fraction: $M_n$ = 11600 g/mol, $M_w$ = 17800 g/mol.

### 2,2'-Bis(2-naphthyl)isophthalophenone



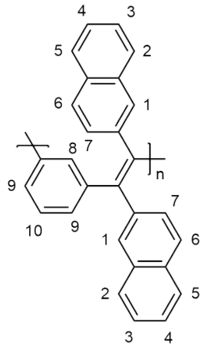
Isophthaloyl chloride (0.10 g, 0.49 mmol, 1.0 eq) was added to naphthalene (0.14 g, 1.08 mmol, 2.2 eq) and aluminium chloride (0.14 g, 1.08 mmol, 2.2 eq) in dichloroethane (5 ml) under argon. The solution was stirred at room temperature for 20 hours. Subsequently cold water was added. Then, the aqueous phase was separated and the organic layer was dried over magnesium sulfate. The solvent was evaporated in vacuo and the crude product was purified by column chromatography (hexane : DCM 1:1) The product was obtained as white solid (0.01 g, 0.04 mmol, 8%) yield.

**$^1$H-NMR** (400 MHz, $CDCl_3$, 300 K): δ [ppm] = 8.33-8.28 (m, 3H, $H_{1,8}$), 8.13 (d, $J$ = 7.7 Hz, 2H, $H_9$), 8.00-7.87 (m, 8H, $H_{2,5,6,7}$), 7.71 (t, $J$=7.7 Hz, 1H, $H_{10}$), 7.62 (t, $J$ = 8.2 Hz, 2H, $H_{3/4}$), 7.58 (t, $J$ = 8.1 Hz, 2H, $H_{3/4}$).

**$^{13}$C-NMR** (101 MHz, $CDCl_3$, 300 K): δ [ppm] = 196.0, 138.4, 135.6, 134.4, 133.6, 132.4, 132.2, 131.4, 129.7, 128.8, 128.7, 128.7, 128.0, 127.1, 125.7.

**MS** (ESI): m/z = 409.1191 calculated for $[C_{28}H_{18}O_2Na]^+$ = 409.1199.

### Poly[1,3-phenylene-1,2-bis(2-naphthyl)vinylene] (Poly-Np2)



Chlorobenzene (10 ml) was added to 2,2’-bis(2-naphthyl)isophthalophenone (0.44 g, 1.15 mmol, 1.0 eq) and phosphorus pentachloride (0.96 g, 4.59 mmol, 4.0 eq) in a Schlenk tube under argon atmosphere. The solution was stirred for 24 hours at 120 °C. Subsequently the solvent, phosphorus oxychloride and excess phosphorus pentachloride were removed by distillation under reduced pressure. The resulting 1,3-bis[dichloro(2-naphthyl)methyl]benzene was used without further purification.

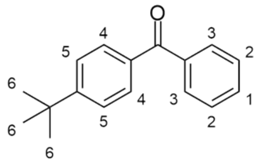
1,3-Bis[dichloro(2-naphthyl)methyl]benzene (0.57 g, 1.15 mmol, 1.0 eq) and dicobalt octacarbonyl (1.07 g, 3.12 mmol, 2.7 eq) where dissolved in chlorobenzene (10 ml) under argon atmosphere. The solution was heated to 100 °C for 50 minutes. Then, 1,2-dichloroethane (10 ml) was added and stirred for further 10 minutes. The polymer was precipitated by addition to acidified (2 M HCl) cold methanol, filtrated and washed with methanol. The crude product was purified by Soxhlet extraction (MeOH, acetone, EtOAc, $CHCl_3$). The ethyl acetate and chloroform fractions were re-precipitated by addition to acidified (2 M HCl) cold methanol. The product was obtained as an orange solid (ethyl acetate fraction: 0.07 g, 0.19 mmol, 16%; chloroform fraction: 0.27 g, 0.75 mmol, 65%).

**$^1$H-NMR** (600 MHz, $C_2D_2Cl_4$, 353 K): δ [ppm] = 7.92-6.41 (m, 18H, $H_{1\text{-}10}$).

**$^{13}$C-NMR** (151 MHz, $C_2D_2Cl_4$, 353 K): δ [ppm] = 143.9, 143.4, 141.6, 141.0, 133.5, 132.4, 130.4, 129.8, 129.5, 128.4, 128.0, 127.8, 127.1, 126.0.

**GPC** (THF). ethyl acetate fraction: $M_n$ = 2600 g/mol, $M_w$ = 3600 g/mol; chloroform fraction: $M_n$ = 5300 g/mol, $M_w$ = 9400 g/mol.

### 1-Benzoyl-4-*tert*-butylbenzene



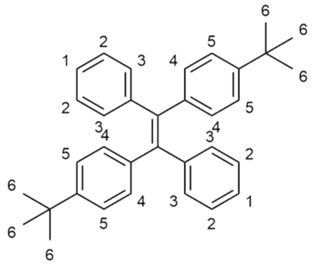
In a dry flask benzoyl chloride (1 ml, 8.68 mmol 1.0 eq) was added to a solution of *tert*-butylbenzene (1.5 ml, 9.72 mmol 1.1 eq) and aluminium chloride (1.39 g, 10.41 mmol, 1.2 eq) in dichloroethane (3 ml) under argon atmosphere. The solution was stirred for 4 hours at room temperature. Subsequently, a large amount of cold water was added and the aqueous phase was extracted with chloroform (3x), dried over magnesium sulfate and the solvent was evaporated in vacuo. The crude product was purified by flash column chromatography (hexane : $CHCl_3$ 1:0 → 8:2). The product was obtained as colourless oil (1.46 g, 6.11 mmol, 70%).

**$^1$H-NMR** (400 MHz, $CDCl_3$, 300 K): δ [ppm] = 7.81 (d, $J$ = 7.0 Hz, 2H, $H_3$), 7.77 (d, $J$ = 8.7 Hz, 2H, $H_4$), 7.58 (t, $J$ = 7.4 Hz, 1H, $H_1$), 7.52-7.43 (m, 4H, $H_{2,5}$), 1.37 (s, 9H, $H_6$).

**$^{13}$C-NMR** (101 MHz, $CDCl_3$, 300 K): δ [ppm] = 196.6, 156.3, 138.1, 135.0, 132.3, 130.3, 130.2, 128.3, 125.4, 35.3, 31.3.

**MS** (ESI): m/z = 261.1249 calculated for $[C_{17}H_{18}ONa]^+$ = 261.1250.

### *E*-1,2-Bis(4-*tert*-butylphenyl)-1,2-diphenylethylene (Mono-t-Bu)



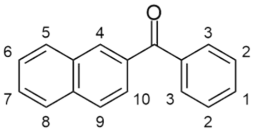
A suspension of zinc (1.60 g, 24.45 mmol, 4.0 eq.) in dry THF (15 ml) was stirred under argon at 0 °C. Titanium tetrachloride (1.4 ml, 12.70 mmol, 2.1 eq.) was added slowly and the ice bath was removed. The mixture was heated to 70 °C for 3.5 hours. Then 1-benzoyl-4-*tert*-butylbenzene (1.46 g, 6.11 mmol, 1.0 eq.) in THF (7 ml) was added. The mixture was stirred at 70 °C for 44 hours. The solution was cooled to room temperature and quenched with a saturated solution of aqueous ammonium chloride. Then, the mixture was extracted with chloroform, the organic phase dried over MgSO4 and the solvent removed by evaporation. The product was obtained as white solid (1.36 g, 3.05 mmol, >99%). The *E/Z*-Isomers were separated by recrystallization from a mixture of hexane and toluene.

**$^1$H-NMR** (400 MHz, $CDCl_3$, 300 K): δ [ppm] = 7.10-7.07 (m, 10H, $H_{1,2/3/4/5}$), 7.06-7.02 (m, 4H, $H_{2/3/4/5}$), 6.92 (d, *J* = 8.5 Hz, 4H, $H_{3/4/5}$), 1.25 (s, 18H, $H_6$).

**$^{13}$C-NMR** (101 MHz, $CDCl_3$, 300 K): δ [ppm] = 149.3, 144.3, 140.9, 140.6, 131.5, 131.1, 127.6, 126.3, 124.5, 34.5, 31.5.

**MS** (ESI): m/z = 467.2635 calculated for $[C_{34}H_{36}Na]^+$ = 467.2709.

### 2-Benzoylnaphthalene



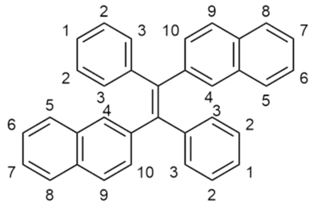
In a dry flask benzoyl chloride (3.0 ml, 26.04 mmol 1.0 eq) was added to a solution of naphthalene (3.67, 28.63 mmol 1.1 eq) and aluminium chloride (4.17 g, 31.27 mmol, 1.2 eq) in chloroform (250 ml) under argon atmosphere. The solution was stirred for 17 hours at room temperature. Subsequently, a large amount of cold water was added and the aqueous phase was extracted with chloroform (3x), the organic phase dried over magnesium sulfate and the solvent removed in vacuo. The crude product was purified by twofold flash column chromatography (hexane : $CH_2Cl_2$ 1:0 → 0:1; hexane : $CH_2Cl_2$ 8:2). The product was obtained as yellow solid (0.73 g, 3.14 mmol, 12%).

**$^1$H-NMR** (400 MHz, $CDCl_3$, 300 K): δ [ppm] = 8.30 (s, 1H, $H_4$), 7.98 (d, *J* = 1.2 Hz, 2H, $H_{9,10}$), 7.96-7.92 (m, 2H, $H_{5,8}$), 7.89 (d, *J* = 8.3 Hz, 2H, $H_3$) 7.69-7.62 (m, 2H, $H_{6,7}$), 7.61-7.51 (m, 3H, $H_{1,2}$).

**$^{13}$C-NMR** (101 MHz, $CDCl_3$, 300 K): δ [ppm] =196.7, 138.0, 135.3, 134.9, 132.4, 132.3, 131.8, 130.1, 129.4, 128.3, 128.3, 128.3, 127.8, 126.8, 125.8.

**MS** (ESI): m/z = 233.0961 calculated for $[C_{17}H_{13}O]^+$ = 233.0961.

### *E*-1,2-Bis(2-naphthyl)-1,2-diphenylethylene (Mono-Np)



A suspension of zinc (0.82 g, 12.57 mmol, 4.0 eq.) in dry THF (12 ml) was stirred under argon at 0 °C. Titanium tetrachloride (0.7 ml, 6.35 mmol, 2.0 eq.) was added slowly and the ice bath was removed. The mixture was heated to 70 °C for 3.5 hours. Then, 2-benzoylnaphthalene (0.73 g, 3.14 mmol, 1.0 eq.) in THF (7 ml) was added. The mixture was stirred at 70 °C for 19 hours. The solution was cooled to room temperature and quenched with a saturated solution of aqueous ammonium chloride. Then, the mixture was extracted with chloroform, the organic phase dried over MgSO4 and the solvent removed by evaporation. The product was obtained as white solid (0.66 g, 1.53 mmol, 97%). The *E/Z*-Isomers were separated by recrystallization from a mixture of hexane and toluene.

**$^1$H-NMR** (400 MHz, $CDCl_3$, 300 K): δ [ppm] = 7.74 (d, *J* = 7.5 Hz, 2H, $H_{5/8}$), 7.63-7.52 (m, 6H, $H_{4,5/8,10}$), 7.44-7.35 (m, 4H, $H_{6,7}$), 7.21 (dd, *J* = 8.4, 1.7 Hz, 2H, $H_9$) 7.14-7.06 (m, 10H, $H_{1-3}$).

**$^{13}$C-NMR** (101 MHz, $CDCl_3$, 300 K): δ [ppm] = 143.9, 141.6, 141.5, 133.4, 132.3, 131.7, 130.7, 129.7, 128.2, 128.0, 127.6, 127.1, 126.8, 125.9, 125.9.

**MS** (ESI): m/z = 455.1789 calculated for $[C_{34}H_{24}Na]^+$ = 455.1770.

**Table SI1. Crystal data and structure refinement of Mono-t-Bu.**

| | | |
|---|---|---|
| Identification code | 12585 | |
| Empirical formula | $C_{34} H_{36}$ | |
| Color | colourless | |
| Formula weight | 444.63 g · mol$^{-1}$ | |
| Temperature | 100(2) K | |
| Wavelength | 1.54178 Å | |
| Crystal system | MONOCLINIC | |
| Space group | **$P2_1/c$, (no. 14)** | |
| Unit cell dimensions | a = 10.6920(2) Å | a= 90°. |
| | b = 19.8135(4) Å | b= 91.4110(10)°. |
| | c = 12.4020(3) Å | g = 90°. |
| Volume | 2626.52(10) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.124 Mg · m$^{-3}$ | |
| Absorption coefficient | 0.469 mm$^{-1}$ | |
| F(000) | 960 e | |
| Crystal size | 0.218 x 0.137 x 0.120 mm$^3$ | |
| q range for data collection | 4.136 to 63.680°. | |
| Index ranges | $-12 \leq h \leq 12$, $-23 \leq k \leq 23$, $-14 \leq l \leq 13$ | |
| Reflections collected | 91198 | |
| Independent reflections | 4322 [$R_{int}$ = 0.1000] | |
| Reflections with I>2s(I) | 3538 | |
| Completeness to q = 63.680° | 100.0 % | |
| Absorption correction | Gaussian | |
| Max. and min. transmission | 0.96 and 0.93 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 4322 / 0 / 314 | |
| Goodness-of-fit on F$^2$ | 1.017 | |
| Final R indices [I>2s(I)] | $R_1$ = 0.0403 | wR$^2$ = 0.0976 |
| R indices (all data) | $R_1$ = 0.0527 | wR$^2$ = 0.1062 |
| Extinction coefficient | 0.00100(18) | |
| Largest diff. peak and hole | 0.2 and -0.2 e · Å$^{-3}$ | |

## Table SI2. Bond lengths [Å] and angles [°] of Mono-t-Bu.

| | | | |
|---|---|---|---|
| C(1)-C(2) | 1.356(2) | C(1)-C(19) | 1.498(2) |
| C(1)-C(25) | 1.498(2) | C(2)-C(3) | 1.495(2) |
| C(2)-C(9) | 1.497(2) | C(3)-C(4) | 1.398(2) |
| C(3)-C(8) | 1.396(2) | C(4)-C(5) | 1.383(2) |
| C(5)-C(6) | 1.382(2) | C(6)-C(7) | 1.384(2) |
| C(7)-C(8) | 1.391(2) | C(9)-C(10) | 1.394(2) |
| C(9)-C(14) | 1.401(2) | C(10)-C(11) | 1.386(2) |
| C(11)-C(12) | 1.396(2) | C(12)-C(13) | 1.392(2) |
| C(12)-C(15) | 1.532(2) | C(13)-C(14) | 1.387(2) |
| C(15)-C(16) | 1.533(2) | C(15)-C(17) | 1.537(2) |
| C(15)-C(18) | 1.527(2) | C(19)-C(20) | 1.398(2) |
| C(19)-C(24) | 1.394(2) | C(20)-C(21) | 1.384(2) |
| C(21)-C(22) | 1.386(2) | C(22)-C(23) | 1.388(2) |
| C(23)-C(24) | 1.386(2) | C(25)-C(26) | 1.392(2) |
| C(25)-C(30) | 1.400(2) | C(26)-C(27) | 1.387(2) |
| C(27)-C(28) | 1.394(2) | C(28)-C(29) | 1.395(2) |
| C(28)-C(31) | 1.536(2) | C(29)-C(30) | 1.386(2) |
| C(31)-C(32) | 1.538(2) | C(31)-C(33) | 1.524(2) |
| C(31)-C(34) | 1.532(2) | | |
| | | | |
| C(2)-C(1)-C(19) | 122.59(13) | C(2)-C(1)-C(25) | 124.15(13) |
| C(25)-C(1)-C(19) | 113.24(12) | C(1)-C(2)-C(3) | 121.54(13) |
| C(1)-C(2)-C(9) | 123.42(13) | C(3)-C(2)-C(9) | 115.01(12) |
| C(4)-C(3)-C(2) | 120.92(13) | C(8)-C(3)-C(2) | 120.64(13) |
| C(8)-C(3)-C(4) | 118.43(14) | C(5)-C(4)-C(3) | 120.68(14) |
| C(6)-C(5)-C(4) | 120.30(15) | C(5)-C(6)-C(7) | 119.94(15) |
| C(6)-C(7)-C(8) | 120.01(15) | C(7)-C(8)-C(3) | 120.58(14) |
| C(10)-C(9)-C(2) | 119.81(13) | C(10)-C(9)-C(14) | 116.64(13) |
| C(14)-C(9)-C(2) | 123.55(13) | C(11)-C(10)-C(9) | 121.65(13) |
| C(10)-C(11)-C(12) | 121.76(14) | C(11)-C(12)-C(15) | 120.47(13) |
| C(13)-C(12)-C(11) | 116.60(13) | C(13)-C(12)-C(15) | 122.91(13) |
| C(14)-C(13)-C(12) | 121.89(14) | C(13)-C(14)-C(9) | 121.43(13) |
| C(12)-C(15)-C(16) | 110.62(12) | C(12)-C(15)-C(17) | 108.16(12) |
| C(16)-C(15)-C(17) | 108.50(14) | C(18)-C(15)-C(12) | 112.27(13) |
| C(18)-C(15)-C(16) | 108.27(14) | C(18)-C(15)-C(17) | 108.95(14) |
| C(20)-C(19)-C(1) | 121.21(13) | C(24)-C(19)-C(1) | 120.42(13) |
| C(24)-C(19)-C(20) | 118.35(14) | C(21)-C(20)-C(19) | 120.77(14) |
| C(20)-C(21)-C(22) | 120.31(14) | C(21)-C(22)-C(23) | 119.53(14) |
| C(24)-C(23)-C(22) | 120.20(15) | C(23)-C(24)-C(19) | 120.81(14) |
| C(26)-C(25)-C(1) | 119.25(13) | C(26)-C(25)-C(30) | 116.77(13) |
| C(30)-C(25)-C(1) | 123.95(13) | C(27)-C(26)-C(25) | 122.01(14) |
| C(26)-C(27)-C(28) | 121.30(14) | C(27)-C(28)-C(29) | 116.78(14) |
| C(27)-C(28)-C(31) | 122.25(14) | C(29)-C(28)-C(31) | 120.89(13) |
| C(30)-C(29)-C(28) | 122.09(14) | C(29)-C(30)-C(25) | 121.05(14) |
| C(28)-C(31)-C(32) | 108.38(13) | C(33)-C(31)-C(28) | 111.53(13) |
| C(33)-C(31)-C(32) | 108.82(15) | C(33)-C(31)-C(34) | 108.79(15) |
| C(34)-C(31)-C(28) | 110.57(13) | C(34)-C(31)-C(32) | 108.69(14) |

**Table SI3. Crystal data and structure refinement of Mono-Np.**

| | | |
|---|---|---|
| Identification code | 12586 | |
| Empirical formula | $C_{34}H_{24}$ | |
| Color | colourless | |
| Formula weight | 432.53 g · mol$^{-1}$ | |
| Temperature | 100(2) K | |
| Wavelength | 1.54178 Å | |
| Crystal system | ORTHORHOMBIC | |
| Space group | **$P2_12_12$, (no. 18)** | |
| Unit cell dimensions | a = 10.6495(3) Å | a= 90°. |
| | b = 20.1283(6) Å | b= 90°. |
| | c = 5.4404(2) Å | g = 90°. |
| Volume | 1166.18(6) Å$^3$ | |
| Z | 2 | |
| Density (calculated) | 1.232 Mg · m$^{-3}$ | |
| Absorption coefficient | 0.527 mm$^{-1}$ | |
| F(000) | 456 e | |
| Crystal size | 0.135 x 0.072 x 0.052 mm$^3$ | |
| q range for data collection | 4.393 to 72.837°. | |
| Index ranges | $-13 \leq h \leq 13$, $-24 \leq k \leq 24$, $-6 \leq l \leq 6$ | |
| Reflections collected | 38509 | |
| Independent reflections | 2291 [$R_{int}$ = 0.1420] | |
| Reflections with I>2s(I) | 1569 | |
| Completeness to q = 67.679° | 99.8 % | |
| Absorption correction | Gaussian | |
| Max. and min. transmission | 0.98 and 0.96 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 2291 / 0 / 155 | |
| Goodness-of-fit on F$^2$ | 1.412 | |
| Final R indices [I>2s(I)] | $R_1$ = 0.1047 | wR$^2$ = 0.2595 |
| R indices (all data) | $R_1$ = 0.1593 | wR$^2$ = 0.3517 |
| Absolute structure parameter | 0.0(7) | |
| Extinction coefficient | 0.11(2) | |
| Largest diff. peak and hole | 0.7 and -0.5 e · Å$^{-3}$ | |

**Table SI4. Bond lengths [Å] and angles [°] of Mono-Np.**

| | | | |
|---|---|---|---|
| C(1)-C(1)* | 1.349(10) | C(1)-C(2) | 1.478(8) |
| C(1)-C(12) | 1.493(8) | C(2)-C(3) | 1.430(8) |
| C(2)-C(11) | 1.361(9) | C(3)-C(4) | 1.363(8) |
| C(4)-C(5) | 1.415(9) | C(5)-C(6) | 1.429(9) |
| C(5)-C(10) | 1.416(8) | C(6)-C(7) | 1.366(10) |
| C(7)-C(8) | 1.406(9) | C(8)-C(9) | 1.379(9) |
| C(9)-C(10) | 1.420(9) | C(10)-C(11) | 1.414(8) |
| C(12)-C(13) | 1.385(9) | C(12)-C(17) | 1.386(9) |
| C(13)-C(14) | 1.382(10) | C(14)-C(15) | 1.375(11) |
| C(15)-C(16) | 1.368(11) | C(16)-C(17) | 1.398(9) |
| | | | |
| C(1)*-C(1)-C(2) | 123.1(7) | C(1)*-C(1)-C(12) | 122.6(6) |
| C(2)-C(1)-C(12) | 114.3(5) | C(3)-C(2)-C(1) | 120.3(5) |
| C(11)-C(2)-C(1) | 122.4(6) | C(11)-C(2)-C(3) | 117.2(5) |
| C(4)-C(3)-C(2) | 122.1(6) | C(3)-C(4)-C(5) | 120.2(6) |
| C(4)-C(5)-C(6) | 122.9(6) | C(4)-C(5)-C(10) | 119.0(6) |
| C(10)-C(5)-C(6) | 118.1(6) | C(7)-C(6)-C(5) | 121.4(6) |
| C(6)-C(7)-C(8) | 120.1(6) | C(9)-C(8)-C(7) | 120.4(6) |
| C(8)-C(9)-C(10) | 120.5(6) | C(5)-C(10)-C(9) | 119.5(6) |
| C(11)-C(10)-C(5) | 118.5(6) | C(11)-C(10)-C(9) | 122.0(6) |
| C(2)-C(11)-C(10) | 123.1(6) | C(13)-C(12)-C(1) | 119.9(6) |
| C(13)-C(12)-C(17) | 117.9(6) | C(17)-C(12)-C(1) | 122.2(6) |
| C(14)-C(13)-C(12) | 121.2(8) | C(15)-C(14)-C(13) | 120.5(8) |
| C(16)-C(15)-C(14) | 119.3(7) | C(15)-C(16)-C(17) | 120.4(7) |
| C(12)-C(17)-C(16) | 120.7(7) | | |

Symmetry transformations used to generate equivalent atoms: * -x-1,-y-1,z

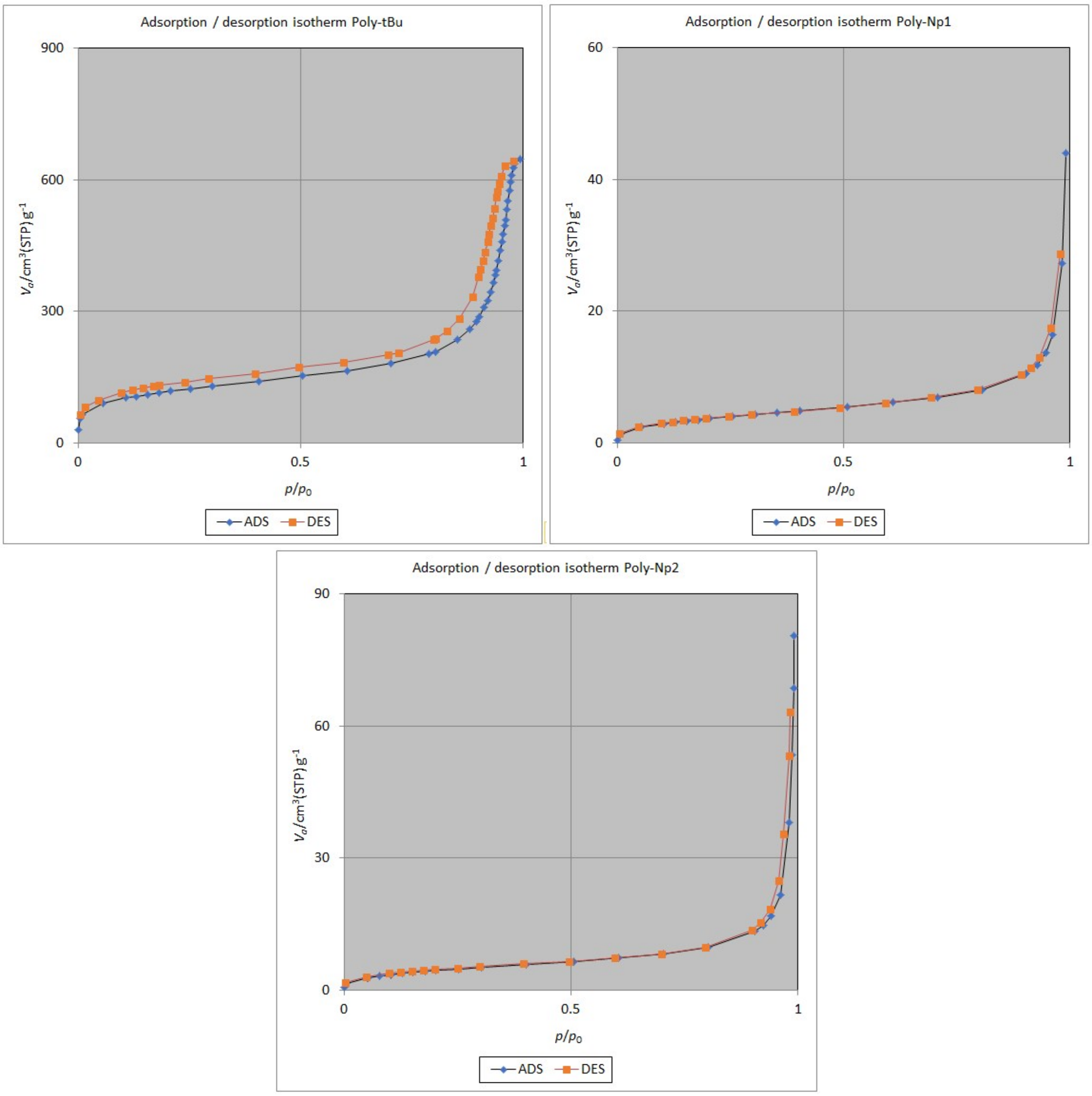


**Figure SI1.** Nitrogen gas adsorption and desorption isotherms for polymers **Poly-t-Bu**, **Poly-Np1** and **Poly-Np2**.

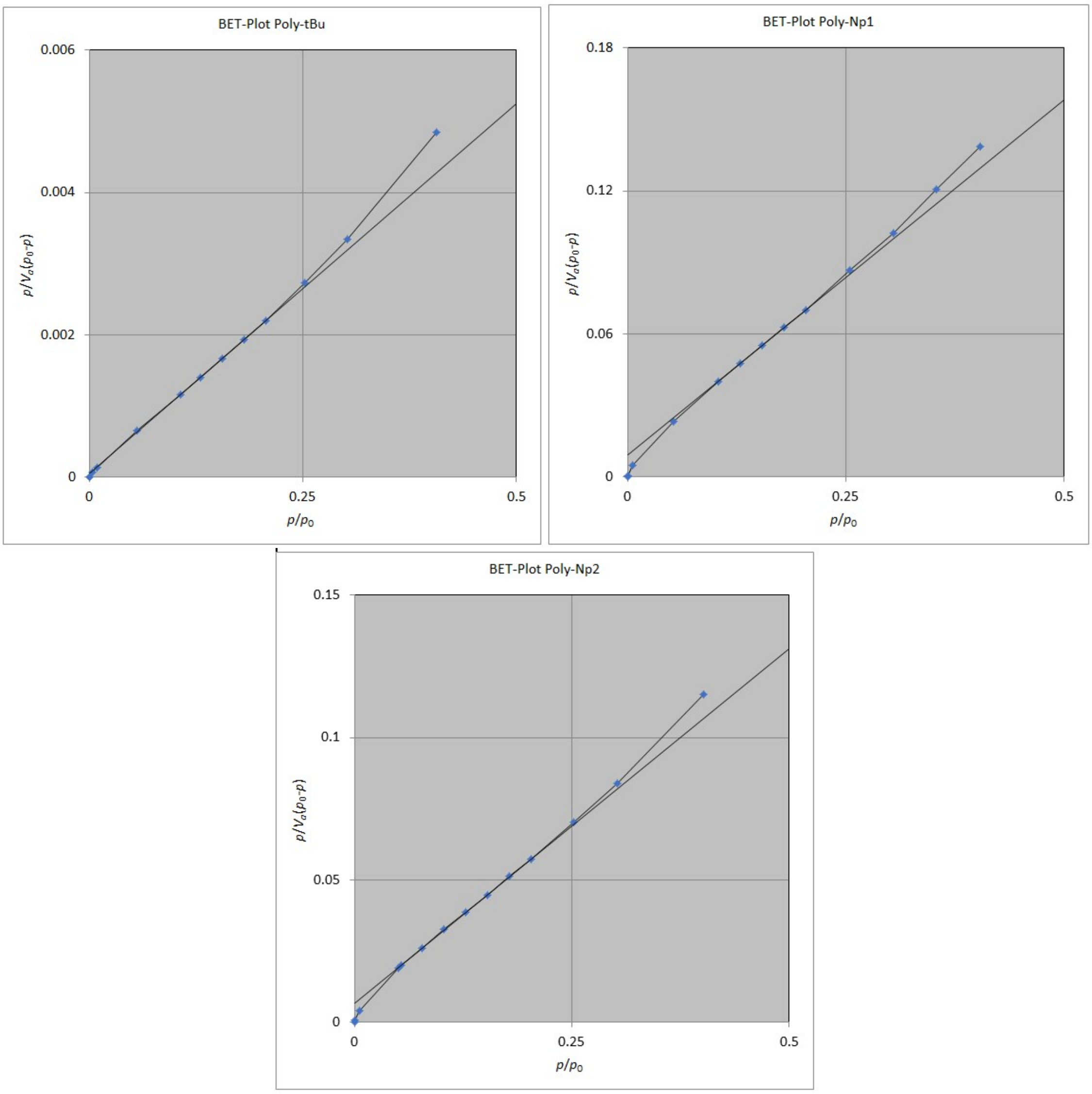
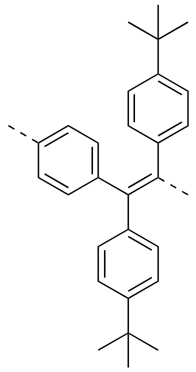
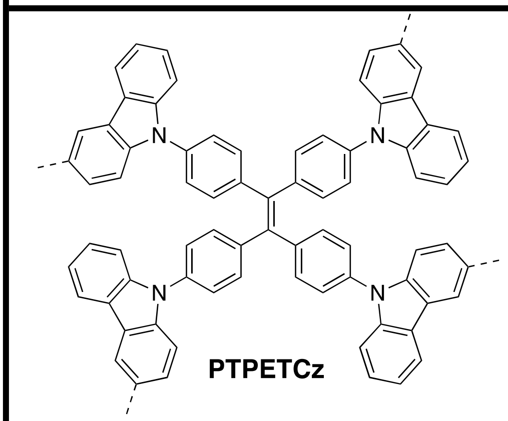
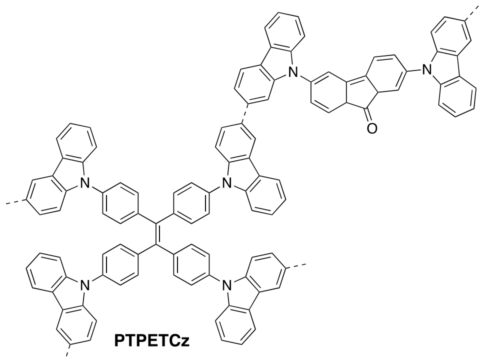
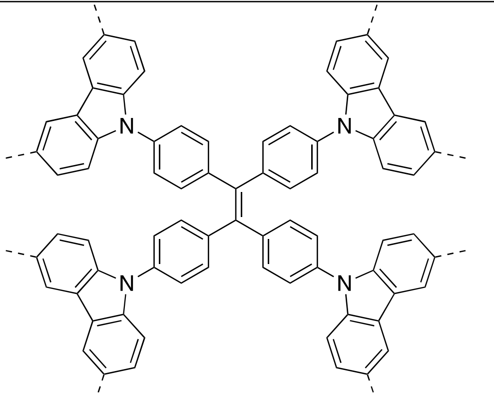
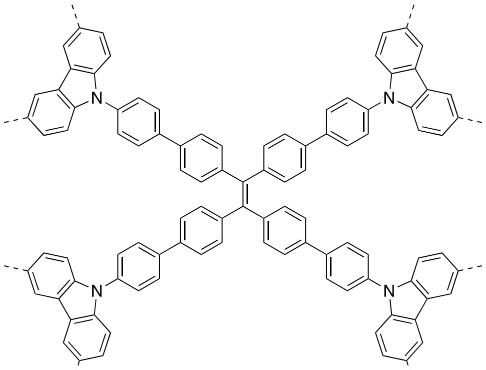
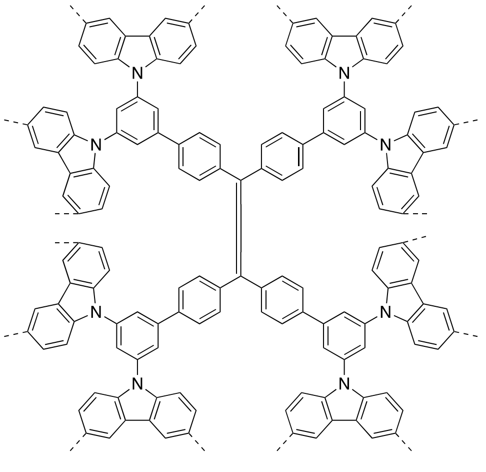
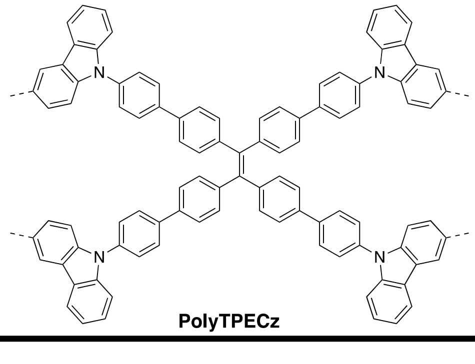
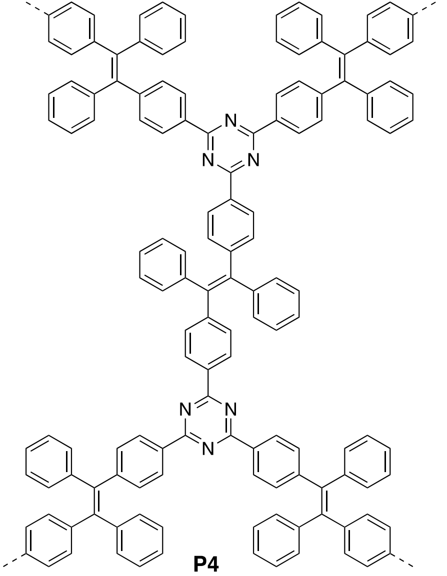
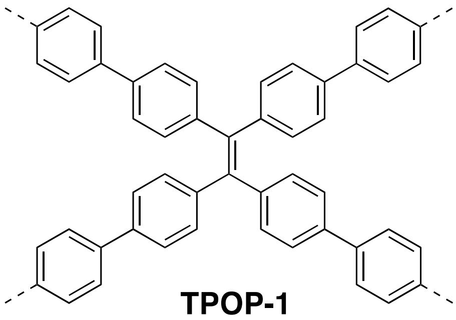
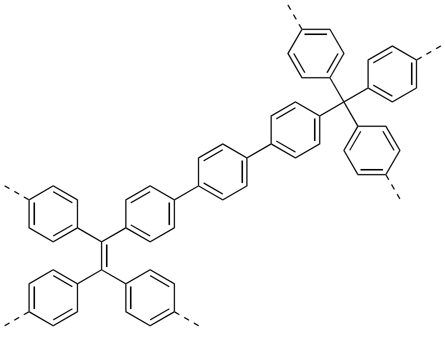
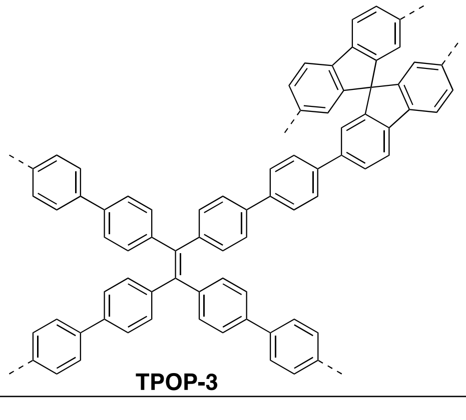


**Figure SI2.** BET surface area fit for polymers **Poly-t-Bu**, **Poly-Np1** and **Poly-Np2**.

**Table SI5.** Comparison of $S_{BET}$ and fluorescence quantum yields of porous TPE based polymers reported on the literature.

| Structure | $S_{BET}$ ($m^2g^{-1}$) | $\phi_F$ (solid state) | Entry |
|---|---|---|---|
|  **Poly-t-Bu** | 412 | 0.64 | This work |
|  **PTPETCz** | 930 | 0.040 (film) | 1 |
|  **PTPETCz** | 509 | 0.019 (film) | |

|  |  |  |  |
|---|---|---|---|
|  **TPETCz** | 1097 | - | 2 |
|  **TPETPTCz** | 1039 | - |  |
|  **TPETPOcCz** | 2203 | - |  |
|  **PolyTPECz** | 1020 | 0.40 (film) | 3 |

|  |  |  |  |
|---|---|---|---|
|  **P4** | 475 | 0.235 (powder) | 4 |
|  **TPOP-1** | 472 | - | 5 |
|  **TPOP-2** | 673 | - |  |
|  **TPOP-3** | 765 | - |  |

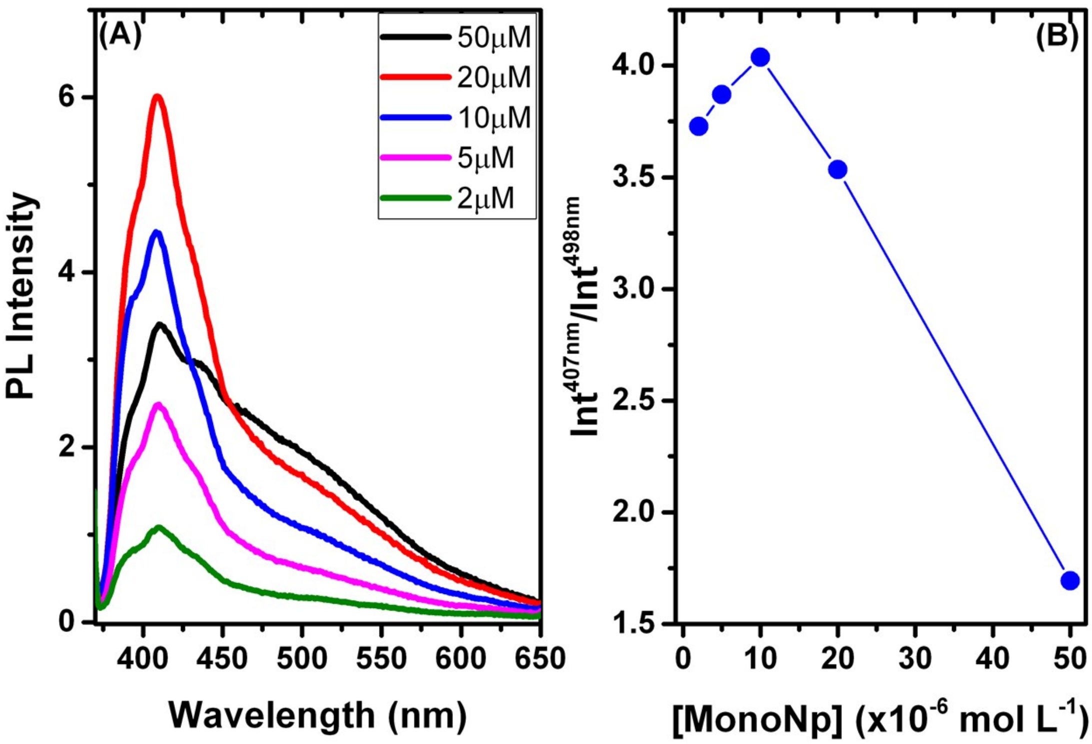


**Figure SI3.** Dependence of the PL spectra of Mono-Np with the concentration in THF. (A) PL spectra of Mono-NP and (B) correlation of the ration of PL intensities at 407 and 498 nm with the increase of concentration of Mono-Np.

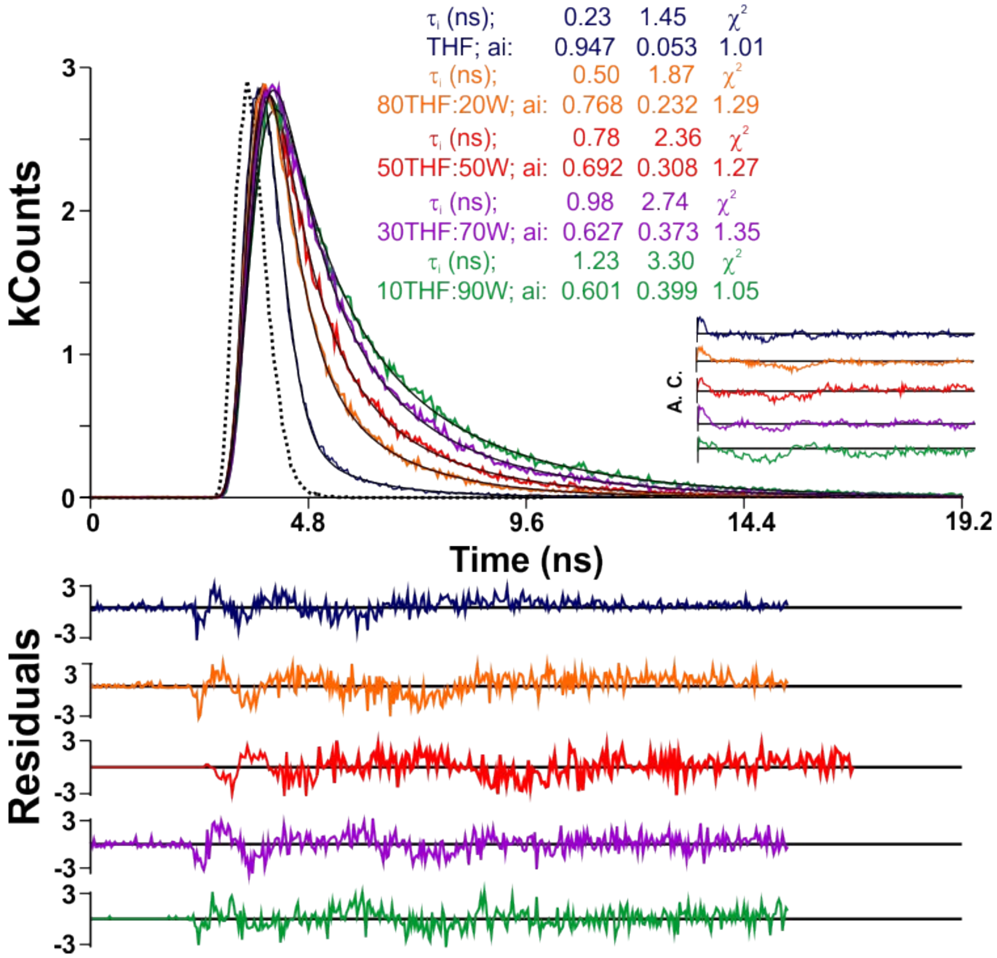


**Figure SI4.** Room temperature fluorescence decays for **Poly-t-Bu** collected with excitation at 339 nm and emission at 525 nm in tetrahydrofuran (THF) solution and in THF:water mixtures. For a better judgment of the quality of the fit, weighted residuals (W.R.), autocorrelation function (A.C.), and χ2 values are also presented. The dashed line corresponds to the instrumental response function.

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