Supplementary Information for

IR Linewidth and Intensity Amplifications of Nitrile Vibrations Report Nuclear-Electronic Couplings and Associated Structural Heterogeneity in Radical Anions

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A. Synthesis



Scheme S1. Synthetic routes for mono nitrile-functionalized ladder-type oligophenylenes. (a) L3PCN. (b) L4PCN. (c) (L3P)₂CN. The conditions are i) Pd(OAc)₂/PCy₃/K₂CO₃/tBuCO₂H; ii) 1-bromohexane/KOtBu; iii) Br₂; iv) CuCN; v) Pd(OAc)₂/SPhos/K₃PO₄; vi) Pd(dppf)Cl₂/KOAc/Bis(pinacolato)diboron.

The synthetic schemes of the target compounds are shown in Fig. S1. The characterization of the compounds L3P (2) 1 , L3PBr (3) 2 , F₁Me₂Br₂ 3 agreed well with previously reported data.

L3PCN (4)

3.50 g (5.24 mmol) of **mono-brominated L3P** (L3PBr) and 1.40 g (15.7 mmol) of CuCN was placed in a 25 mL reaction vessel and purged for 30 minutes with nitrogen. 29 mL of dried and deoxygenated DMF (0.18 M) was added to the reaction flask and heated to 150 °C for 24 hours. The reaction was then quenched with ammonium chloride-water solution and poured over equal parts ammonium chloride-water solution and dichloromethane (DCM). It was washed with DCM five times. The organic components were dried with MgSO₄, filtered, and the organic solvent was evaporated under reduced pressure. The crude was purified via column chromatography on silica gel (v/v 1:4 DCM/hexanes) to afford the product as a yellow crystalline solid (1.80 g, 55.8%). ¹H NMR (CD₂Cl₂, 400.15 MHz) δ 7.83-7.76 (m, 2H), 7.72-7.64 (m, 4H), 7.39-7.30 (m, 3H), 2.09-2.02 (m, 8H), 1.15-0.93 (m, 24H), 0.79-0.67 (m, 12H), 0.67-0.49 (8H); ¹³C NMR (CD₂Cl₂, 400.15 MHz) δ 152.33, 151.88, 151.46, 151.04, 146.74, 143.12, 141.50, 139.15, 131.73, 127.87, 127.32, 127.04, 123.53, 120.53, 120.35, 120.23, 115.62, 114.63, 109.79, 55.73, 55.39, 41.07, 40.87, 32.06, 30.16, 30.09, 24.25, 23.02, 14.27.

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To a round-bottom flask containing the compound $F_1Me_2Br_2$ (4.67 g, 8.96 mmol), 2chlorophenylboronic acid (3.18 g, 19.7 mmol), potassium phosphate tribasic (K₃PO₄, 7.83 g, 36.1 mmol), Pd(OAc)₂ (0.246 g, 1.08 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos, 0.912 g, 2.18 mmol), 37.4 mL of toluene and 1.87 mL of distilled water were added. The reaction mixture was deoxygenated and then stirred at 90 °C for 8 h under Ar. The mixture was cooled down and quenched with water (100 mL). The mixture was extracted with DCM and the organic layer was washed with brine three times and dried over MgSO₄. After filtration and removal of the solvents *in vacuo*, the crude mixture was purified by column chromatography on silica gel (hexanes) to afford the title compound as a colorless oily liquid (4.47 g, 85.4%). ¹H NMR (CD₂Cl₂, 400 MHz) δ 7.64 (s, 2H), 7.52-7.50 (d, 2H), 7.33-7.35 (m, 6H), 7.12 (s, 2H), 2.20 (s, 6H), 1.95-1.87 (m, 4H), 1.15-1.04 (m, 12 H), 0.80-0.70 (m, 10 H). ¹³C NMR (CD₂Cl₂, 100 MHz) δ 149.04, 141.78, 141.23, 138.72, 135.13, 134.10, 134.08, 131.94, 131.92, 129.94, 129.93, 129.09, 127.17, 127.15, 124.78, 121.41, 55.33, 40.80, 40.68, 32.05, 30.18, 30.15, 30.12, 24.46, 24.33, 24.20, 23.10, 23.05, 23.00, 20.35, 14.32.

dihex-L4P (6)

To a round-bottom flask containing compound **5** (4.03 g, 6.91 mmol), K₂CO₃ (5.76 g, 41.7 mmol), Pd(OAc)₂ (0.191 g, 0.833 mmol), PCy₃ (0.466 g, 1.66 mmol), pivalic acid (tBuCO₂H, 1.43g, 13.8 mmol), and 30 mL of dimethylacetamide (DMA) were added. The reaction mixture was deoxygenated and then stirred at 145 °C for overnight under Ar. The mixture was cooled down and quenched with water (200 mL). The mixture was extracted with DCM. The organic layer was collected and washed with brine three times and dried over MgSO₄. After filtration and removal of the solvents *in vacuo*, the crude mixture was purified by column chromatography on silica gel (hexanes) to afford the title compound as a white solid (0.400 g, 11.4%). ¹H NMR (CD₂Cl₂, 400 MHz) δ 7.91 (s, 2H), 7.86-7.84 (d, 2H), 7.78 (s, 2H), 7.58-7.56 (d, 2H), 7.42-7.38 (t, 2H), 7.32-7.28 (t, 2H), 3.98 (s, 4H), 2.15-2.10 (m, 4H), 1.11-0.97 (m, 12H), 0.72-0.63 (m, 10 H). ¹³C NMR (CD₂Cl₂, 100 MHz) δ 150.97, 144.41, 143.11, 142.58, 141.46, 141.18, 127.25, 126.90, 125.61, 120.06, 116.47, 114.78, 55.09, 41.60, 37.33, 32.17, 30.34, 30.27, 24.45, 23.16, 14.29.

dihex-L4PBr (7)

Compound **6** (1.13 g, 2.20 mmol) was dissolved in 36 mL of DCM and stirred at 0 °C for 10 min. FeCl₃ (0.0205 g, 0.13 mmol) was added to the mixture and stirred for another 10 min. Bromine (Br₂, 0.107 mL, 2.09 mmol) was added dropwise to the reaction mixture. The resulting solution was stirred at 0 °C for 2 h. The reaction mixture was poured into 150 mL of water and extracted with 150 mL of DCM. The organic layer was washed with sodium thiosulfate (10%) and brine. The organic layer was collected and dried over MgSO₄. After filtration, the solvent was removed *in vacuo*. The crude product was purified by column chromatography on silica gel (hexanes) to afford a light yellow solid (0.354 g, 27.1%). ¹H NMR (CDCl₃, 400 MHz) δ 7.87-7.85 (d, 2H), 7.74-7.69 (m, 5H), 7.57-7.53 (m, 2H), 7.44-7.40 (t, 1H), 7.33-7.29 (t, 1H), 3.97-3.95 (s, 4H), 2.11-2.07 (m, 4H), 1.12-0.97 (m, 12H), 0.79-0.68 (m, 10 H). ¹³C NMR (CDCl₃, 100 MHz) δ 150.86, 150.60, 145.92, 143.96, 142.63, 142.32, 142.27, 142.23, 141.35, 141.32, 141.26, 140.98, 140.53, 140.24, 140.01, 130.07, 130.04, 128.46, 126.95, 126.62, 125.29, 121.11, 121.07, 120.29, 120.18, 119.86, 116.28, 116.17, 114.41, 114.35, 54.78, 54.74, 41.30, 41.25, 37.01, 36.86, 31.74, 30.00, 29.98, 23.99, 23.86, 14.30.

L4PBr (8)

To a round-bottom flask containing compound **7** (0.320 g, 0.543 mmol) in 120 mL of THF, potassium tert-butoxide (KOtBu, 0.529 g, 4.62 mmol) was added. The resulting mixture was deoxygenated by bubbling with Ar and stirred for 30 min. 1-Bromohexane (0.670 mL, 4.68 mmol) was added dropwise to the mixture and then stirred for 3 h at room temperature under Ar. The reaction mixture was concentrated to about 50 mL in vacuo, and poured into 120 mL of water and extracted with ethyl acetate (300 mL). The organic layer was collected and washed with brine three times, and then dried over MgSO4. After filtration and removal of the solvents in vacuo, the crude mixture was purified by column chromatography on silica gel (hexanes) to afford the title compound as a light yellow solid (0.439 g, 87.3%). ¹H NMR (CDCl₃, 400 MHz) δ 7.77-7.76 (d, 1H), 7.66-7.58 (m, 5H), 7.49-7.48 (d, 1H), 7.37-7.34 (t, 1H), 7.31-7.29 (d, 1H), 2.07-1.97 (m, 12H), 1.07-1.00 (m, 36H), 0.74-0.69 (m, 30H), ¹³C NMR (CDCl₃, 100 MHz) δ 153.50, 151.26, 150.90, 150.65, 150.31, 149.98, 149.90, 141.74, 141.46, 140.97, 140.89, 140.79, 140.62, 139.49, 139.24, 129.99, 129.96, 126.85, 126.79, 126.34, 123.14, 120.96, 120.91, 120.67, 120.54, 119.56, 114.18, 114.14, 114.10, 113.86, 113.76, 55.31, 54.93, 54.62, 54.57, 41.14, 41.08, 40.74, 40.65, 31.75, 31.73, 31.62, 29.89, 29.87, 29.79, 23.91, 23.86, 23.81, 22.70, 14.16.

L4PCN (9)

In a 10 mL reaction vessel, 0.250 g (0.270 mmol) of **L4PBr** and 63 mg (0.70 mmol) of CuCN were placed and immediately purged with N₂ for 30 minutes. Thereafter, 1.50 mL (0.180 M) of DMF was added to the reaction and heated at 150 °C for 17 hours. Ammonium chloride-water solution was used to quench the reaction, which was then poured over equal amounts of brine and DCM in a separatory funnel and washed five times with DCM. The organic components were combined and then washed with deionized water once. The organic component was dried with MgSO4, filtered, and the organic solvent was evaporated under reduced pressure. The crude was purified via running column chromatography twice on silica gel (v/v 1:2 DCM/hexanes, then 1:6 DCM/hexanes) to afford the product as a yellow crystalline solid (120 mg, 51.1%): ¹H NMR (CD₂Cl₂, 300.15 MHz) δ 7.84-7.65 (m, 8H), 7.39-7.28 (m, 3H), 2.14-2.05 (m, 12H), 1.18-0.94 (m, 36H), 0.79-0.55 (m, 30H); ¹³C NMR (CD₂Cl₂, 300.15 MHz) δ 152.37, 151.69, 151.57, 151.37, 150.76, 146.91, 143.58, 142.00, 141.64, 140.94, 138.86, 131.79, 127.38, 127.08, 123.52, 120.59,

120.31, 119.95, 115.62, 114.58, 114.29, 109.71, 55.78, 55.37, 55.14, 41.41, 41.16, 40.92, 32.13, 32.07, 30.20, 24.36, 23.05, 14.30.

BrL3PCN (10)

In a 50 mL reaction vessel, 1.50 g (2.44 mmol) of **L3PCN** was placed. In an air atmosphere, 13.9 mL (0.174 M) of DCM was added and stirred at room temperature. Thereafter, 6.8 mg (0.027 mmol) of diatomic iodine was added. Shortly after, 0.128 mL (2.48 mmol) of diatomic bromine was added and the reaction was left to stir overnight at room temperature. Three iterations of solvent removal (using only DCM) were performed to remove excess bromine and iodine. The remaining solid was recrystallized in ethanol to afford a white crystalline solid (1.63 g, 88.9%): ¹H NMR (CD₂Cl₂, 400.15 MHz) δ 7.84-7.82 (d, 2H, *J* = 7.8 Hz), 7.74-7.62 (m, 5H), 7.54-7.47 (m, 2H), 2.11-1.96 (m, 8H), 1.13-0.95 (m, 24H), 0.78-0.69 (m, 12H), 0.68-0.52 (m, 8H); ¹³C NMR (CD₂Cl₂, 400.15 MHz) δ 154.23, 152.41, 151.75, 150.79, 146.54, 141.99, 140.70, 139.69, 131.80, 130.51, 127.14, 126.88, 121.81, 121.71, 120.53, 120.46, 115.71, 114.85, 110.12, 55.84, 41.02, 40.86, 32.07, 30.13, 30.09, 24.28, 23.05, 23.03, 14.28.

L3PBpin (11)

In a 25 mL reaction vessel, 1.40 g (2.10 mmol) of **L3PBr**, 1.06 g (4.19 mmol) of bis(pinacolato)diboron, 0.092 g (0.13 mmol) of Pd(dppf)Cl₂ and 0.411 g (4.19 mmol) of potassium acetate (KOAc) were combined and immediately purged with N₂ three times. Then, 6.5 mL of dried and deoxygenated DMF was added and the reaction was refluxed and stirred at 80 °C for 24 hours. Thereafter, the reaction solution was poured over brine and washed with equal parts DCM three times. The organic layers were combined, dried with MgSO₄, and filtered. The solvent was removed under reduced pressure. The product was purified via column chromatography on silica gel (v/v 1:3 DCM/hexanes) to afford a white crystalline solid (0.450 g, 27.8%): ¹H NMR (CD₂Cl₂, 400.15 MHz) δ 7.78-7.72 (m, 4H), 7.70-7.68 (d, 2H, *J* = 7.0 Hz), 7.38-7.28 (m, 3H), 2.09-2.02 (m, 8H), 2.11-1.99 (m, 8H), 1.38 (s, 12H), 1.13-0.95 (m, 24H), 0.79-0.68 (m, 12H), 0.67-0.52 (m, 8H); ¹³C NMR (CD₂Cl₂, 400.15 MHz) δ 151.82, 151.23, 150.88, 150.61, 145.14, 142.05, 141.79, 140.97, 134.05, 129.30, 127.34, 127. 22, 123.49, 119.94, 119.17, 114.95, 114.57, 84.26, 55.34, 41.17, 41.12, 32.13, 30.67, 30.24, 25.34, 24.35, 23.07, 14.30.

$(L3P)_2CN(12)$

In a 10 mL reaction vessel, 0.356 g (0.474 mmol) of **BrL3PCN**, 0.440 g (0.569 mmol) of **L3PBpin**, 10.7 mg (0.0477 mmol) of Pd(OAc)₂, 42.9 mg (0.105 mmol) of SPhos, and 0.261 g (1.23 mmol) of K₃PO₄ were combined and immediately purged with N₂ three times. Thereafter, 3.2 mL (0.15 M) of deoxygenated toluene with added drops of water was transferred to the reaction vessel. The reaction was then stirred and heated to 85 °C for 20 hours. Thereafter, the reaction was poured over brine and washed with equal parts DCM three times. The organic layers were combined, dried with MgSO₄, and filtered. The solvent was removed under reduced pressure. The product was purified via flash chromatography on silica gel (v/v 1:9 DCM/hexanes) to afford a lime-green crystalline solid (0.175 g, 28.0%): ¹H NMR (CD₂Cl₂, 400.15 MHz) δ 7.92-7.81 (m, 3H), 7.80-7.62 (m, 11H), 7.42-7.27 (m, 3H), 2.24-1.99 (m, 16H), 1.16-0.97 (m, 48H), 0.81-0.53 (m, 40H); ¹³C NMR (CD₂Cl₂, 400.15 MHz) δ 152.74, 152.56, 152.42, 151.76, 151.68, 151.46, 150.96, 150.76, 146.81, 142.91, 142.13, 141.56, 141.40, 141.34, 140.85, 140.74, 140.45, 139.22, 131.80, 130.52, 127.24, 127.11, 126.59, 126.47, 123.50, 121.95, 121.90, 120.59, 120.41, 120.16, 119.88, 115.72, 114.75, 114.63, 109.88, 55.83, 55.65, 55.54, 55.36, 41.21, 40.93, 32.15, 32.10, 30.27, 30.19, 30.15, 24.39, 24.32, 23.09, 23.06, 14.32.

B. Details of X-ray Crystals

The structure of L3P crystallizes in the centrosymmetric triclinic space group P-1 and encompasses half of the molecule as the contents of its asymmetric unit. Close inspection of the interplanar distances, as judged by the distance between C6 atoms from symmetry-equivalent molecules of L3P, showed that those planes are separated by distances of 3.359(2) Å. The saturated alkyl chains which propagate along the crystallographic *c*-axis when looking into the *ac*-plane show no signs of positional disorder. The propagating alkyl chains effectively insulate the aromatic cores along the same direction; however, no significant overlap between those aromatic regions was observed.



Fig. B1. Anisotropic displacement ellipsoid plot of L3P with ellipsoids set to the 50% probability level. The asymmetric unit is numbered and hydrogen atoms have been removed for the sake of clarity.

The structure of L3PCN was solved in the non-centrosymmetric monoclinic space group Pn and contained two independent molecules within the asymmetric unit. As with L3P, the saturated alkyl chains show no signs of positional disorder and prevent the aromatic cores from experiencing significant π -orbital overlap. Due to symmetry, the molecules pack in such a way that they form square grids when looking into the *bc*-plane with borders consisting of the aromatic moieties of the molecules with an approximate area of ~210 Å². These grids propagate down the full length of the *a*-axis forming channels where interstitial solvent molecules might reside if not blocked by the steric bulk imparted by the alkyl chains.

Compound	L3P	L3PCN
CCDC code	209703	209702
Formula	C44H62	C45H61N
Formula weight	594.26	615.94
Temp.	100(2)	89.9(5)
Space group	P-1	Pn
a, Å	8.2606(2)	9.2000(3)
b, Å	10.6753(2)	21.2470(10)
c, Å	11.8869(2)	19.8882(8)
α, deg	92.805(2)	90.00
β, deg	109.769(2)	101.072(4)
γ, deg	104.294(2)	90.00
volume, Å ³	945.78(4)	3815.2(3)
Z	1	4
Density (calculated), mg/m ³	1.038	1.072
μ, mm ⁻¹	0.423	0.446
Scan	ω scan	ω scan
heta range for data collection, deg	5.829-66.590	4.531-61.164
Reflections measured	8853	19901
Independent observed reflns.	3337	9044
Independent reflns. [<i>I</i> >2σ]	3082	6478
Data/restraints/parameters	3337/0/202	9044/2/838
R _{int}	0.0160	0.0500
Final <i>R</i> Indices [<i>I</i> >2σ]	$R_1 = 0.0353,$	$R_1 = 0.0669,$
	wR2 = 0.0924	wR2 = 0.1733
R Indices (all data)	$R_1 = 0.0380,$	$R_1 = 0.0964,$
	wR2 = 0.0943	wR2 = 0.1954
Goodness-of-fit on F^2	1.049	1.033
Flack parameter		0.3(17)

Table B1. Single crystal X-ray data for L3P and L3PCN.



Fig. S1. FTIR spectra of neutral molecules in THF.



Fig. S2. Dependence of the $v(C \equiv N)$ IR linewidths on molecular weight for the neutral forms of the series of nitrile-functionalized molecules under investigation (Chart 1 and 1-cyanonapthalene and 9-cyanoanthracene). FWHMs were obtained from fits of the bands to a Voigt function. The Lorentzian widths were also taken from the parameters of the Voigt fits.



Fig. S3. Relative population (left axis) and energy (right axis) vs the dihedral angle, obtained from DFT calculations of (a) the $F_2CN^{\bullet-}$ radical anion and (b) the F_2CN neutral. Structures are optimized at each fixed dihedral angle. Relative population was estimated by the Boltzmann distribution for room temperature (295 K).



Fig. S4. The DFT optimized structures of the neutral forms of (a) L4PCN and (b) F₂CN.



vs total polarizability (Bohr³). (b) Correlation between the total intensity of the $v(C \equiv N)$ IR bands of the neutral species vs dipole moment (Debye). Total polarizabilities and dipole moments are based on DFT calculations. The experimental data are in THF.

Fig. S5. (a) Correlation between the total intensity of the $v(C \equiv N)$ IR bands of the neutral species



Fig. S6. The absorption spectra of the radical anions of L3PCN and L4PCN in THF obtained by pulse radiolysis. The uncertainty of the extinction coefficient is ± 20 %.

D. Supplemental Tables

			Neutral			Anion	
	Number	Number					
Namo	of	of	v	FWHM ^a	ε	ν	FWHM ^a
Inallie	Phenyl	Dihedral	(cm^{-1})	(cm^{-1})	$(M^{-1} cm^{-1})$	(cm^{-1})	(cm^{-1})
	Ring	Angles					
PhCN	1	0	2228	7.0	140	2073	12.2
6CB	2	1	2226	6.7	300	2106	18.8
F ₁ CN	2	0	2223	6.1	370	2101	21.8
L3PCN	3	0	2221	6.2	520	2116	24.4
F ₂ CN	4	1	2222	6.4	480	2125	31.3
L4PCN	4	0	2221	6.1	600	2123	27.0
F ₃ CN	6	2	2223	6.5	540	2129	38.4
(L3P) ₂ CN	6	1	2221	6.2	750	2125	31.9

Table S1. Observed $v(C \equiv N)$ of Neutral and Anionic Forms of Mononitrile-Functionalized Aryl Compounds in DMF

^a FWHM = full width at half maximum. The values reported here are obtained from fits of the bands to a Voigt function.

Table S2. Computed $v(C \equiv N)$ of Neutral and Anionic Forms of Mononitrile-Functionalized Aryl Compounds at Optimized Geometries in THF

				Neutral		Anion		
Name	Number of Phenyl Rings	Number of Dihedral Angles	Geometry	ν (cm ⁻¹)	IR Intensities (km/mol)	<i>v</i> (cm ⁻¹)	IR Intensities (km/mol)	Δv^{a} (cm ⁻¹)
PhCN	1	0	Optimized	2308.2	103.3	2102.6	1577.0	-205.6
6CB	2	1	Optimized	2263.3	181.6	2147.8	3040.1	-115.6
F ₁ CN	2	0	Optimized	2300.9	193.5	2132.4	3938.0	-168.5
5CT	3	2	Optimized	2305.1	183.4	2154.0	6784.1	-151.2
L3PCN	3	0	Optimized	2299.8	243.9	2148.1	7229.4	-151.7
E.CN	4	1	Optimized	2300.7	232.0	2156.4	8715.7	-144.3
F2CIN		4	1	$arphi=0^{ m o}$	2259.4	287.8	2161.9	10755.7
L4PCN	4	0	Optimized	2299.8	259.6	2156.4	9996.3	-143.4
F ₃ CN	6	2	Optimized	2301.2	236.0	2161.5	10033.0	-139.7
$(\mathbf{I}, \mathbf{2D})$, \mathbf{CN}	6	6 1	Optimized	2299.8	258.5	2160.1	10740.3	-139.8
$(LSP)_2CN$			$arphi=0^{ m o}$	2258.7	325.9	2175.3	18412.2	-83.4

 $^{a}\Delta v = v_{anion} - v_{neutral}$

			Neutral		Anion	
	Number of	Number of	Angle 1	Angle 2	Angle 1	Angle 2
Name	Phenyl	Dihedral	Close to	Away from	Close to	Away from
	Rings	Angles	CN (°)	CN (°)	CN (°)	CN (°)
PhCN	1	0				
6CB	2	1	34.85		11.71	
F ₁ CN	2	0				
5CT	3	2	34.75	35.01	12.88	25.18
L3PCN	3	0				
F ₂ CN	4	1	35.85		23.89	
L4PCN	4	0				
F ₃ CN	6	2	36.24	35.85	23.69	32.91
(L3P) ₂ CN	6	1	36.30		29.68	

Table S3. Computed Dihedral Angles of Neutral and Anionic Forms of Mononitrile-Functionalized Aryl Compounds at Optimized Geometries in THF

E. References

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