LFER Correlation of ^{13}C Chemical Shift in Para-Substituted Phenyl Isocyanide: Implications for Formation of a Unique Polymer

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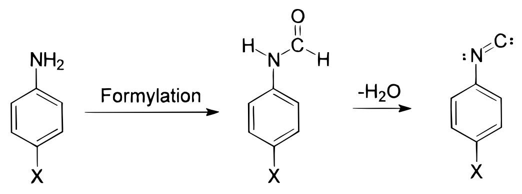
Introduction

The phrase “linear free energy relationship” (LFER) as applied in organic chemistry to the Hammett equation grew out of the seminal studies of Hammett.[1] Normally such an LFER refers to a linear correlation where a chemical or spectroscopic process is used as a probe. The resultant equilibrium, rate constants, or excitation energies for the processes are then correlated in the presence of a variety of perturbations. As a consequence, substituent electronic perturbation effects that alter these processes can be studied from the point of view of the substituents, the Hammett σ constants, or the reactions of interest through the Hammett ρ constant. Recently, σ substituent electronic effects have been probed in the ground state through the aegis of NMR chemical shift correlations.[2] In these studies neither a chemical reaction nor a spectroscopic excitation of electronic states was monitored. Instead, the probe involved a nuclear excitation immersed in a magnetic field where the chemical shift change that occurred in the presence of a variety of substituents was monitored to determine linearity.

As an adjunct to some studies our group has been involved with recently,[3] we needed to prepare a series of *p*-substituted phenyl isocyanide (*p*-X-φ-NC) derivatives. Convenience of preparation and purity of sample were of prime importance. Our intent was to polymerize the *p*-X-φ-NC derivatives, using the standard conditions we have developed, so that the parent polymer could be studied in the “as prepared”, state as we have done with the parent phenyl isocyanide.[3] Easy access to substantial quantities of the well-characterized and pure monomer presumably would lead to a polymer with few impurities. In the course of these investigations, we noticed that the derived *p*-X-φ-NC compounds exhibited ^{13}C NMR spectra that were easy to interpret and, furthermore, the isocyanide group seemed to be an interesting probe of the electronic demand that the various substituents were exerting. Thus, we offer this report in testimony to the observation that the isocyano-carbon is able to probe substituent electronic effects in a linear manner. There was, however, one major exception that did not correlate linearly. Our LFER analysis implied that this one exception, the *p*-hydroxy example, is involved in an interesting hydrogen-bonded equilibrium that may be the direct precursor to a polymerization process that is rather unique. As a further result, then, we note this one exception as an example of the logical power that LFER analysis can provide.

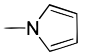
Scheme 1



1 2 3

a) X = H
b) X = NO_2
c) X = CO_2CH_3
d) X = $NHCOCH_3$
e) X = OTBDMS[a]
f) X = N-pyrrolo[b]
g) X = OCH_3
h) X = Cl
i) X = CH_3
j) X = NH_2
k) X = OH
l) X = $O^- H^+$ [c]

[a] OTBDMS = t-butyldimethylsiloxy

[b] N-pyrrolo =


[c] Ionized phenoxy (see Scheme 2)

Results and Discussion

Preparations of the requisite *p*-substituted phenyl isocyanide derivatives were generally performed[5] as shown in Scheme 1. Some of the isocyanide compounds were previously known in the literature,[6] and these compounds were prepared as specified. The remaining isocyano derivatives, **3c**,**d**−**f**,**k**, were synthesized in good yield using the mixed anhydride[7] method for the formylation step (**1** → **2**) and then applying the method of Skorna and Ugi[8] to convert **2** → **3** by dehydration. Attempts to prepare *p*-hydroxyphenyl isocyanide, **3k**, by these, or other,[9] direct methods were unsuccessful, and thus we found it necessary to deprotect the derivative **3e** utilizing $(n\text{-Bu})_4NF$ in THF as a desilylation agent.[10] Table 1 gives some relevant information that can be utilized to characterize these isocyano compounds. The preparation and reactivity of isonitriles, in general, have been extensively reviewed.[11]

Table 1 lists data available for the series of para-substituted phenyl isocyanide compounds examined in this study, except for **3l**. A correlation of the data taken from the first two columns of Table 1 is displayed as Figure 1. The chemical shift difference between the isocyano carbon (C^o) of a substituted derivative and that of the unsubstituted phenyl isocyanide (**3a**) is plotted as the abscissa of Figure 1. The ordinate contains the consensus Hammett σ constants[12] for the common sub-

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[1] Hammett, L. P. *J. Am. Chem. Soc.* **1937**, *59*, 96.

[2] Craik, D. J.; Brownlee, R. T. C. *Prog. Phys. Org. Chem.* **1983**, *14*, 1.

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Table 1. NMR and IR data for the isocyano group in the compounds studied[a]

derivative	σ^a	$\delta(C^o)^b$	$J(C^1-N)^c$	$\nu(NC)^d$
3a	0.00[e]	165.7[f]	13.2[f]	2127[f]
3b	0.78	170.2	12.0	2130
3c	0.39	167.2	12.4	2127
3d	−0.32	163.0	11.2	2124
3e	−0.31[e]	163.2	13.9	2123
3f	−0.02[e]	165.2	13.8	2122
3g	−0.27	164.2[f]	12.4[f]	2126[f]
3h	0.23	167.2[f]	10.0[f]	2126[f]
3i	−0.17	165.1[f]	13.4[f]	2126[f]
3j	−0.66	161.1	14.4	2129
3k	−0.37	161.4	12.6	2124

[a] Hine, J. *Physical Organic Chemistry*; Mc-Graw-Hill, New York, 1962; p 87 and ref 12. [b] C° chemical shift for compounds **3** in ppm downfield from TMS. [c] Coupling constant for the isocyanonitrogen and the ipso (C^1) carbon in hertz. [d] IR stretching frequency of the isocyano group in cm^{-1} determined as either a neat liquid film or KBr pellets. [e] Values determined from Figure 1 or in the case of **3a** set at 0.00. [f] See ref 13. [g] Attempts to correlate the coupling constant or the IR stretching frequency to the Hammett σ constant were not satifactory (see ref 9 for correlation of ν vs the absolute value of σ).

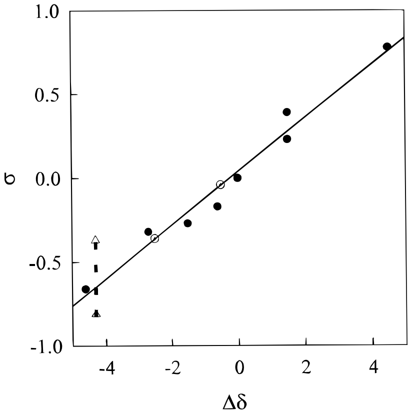
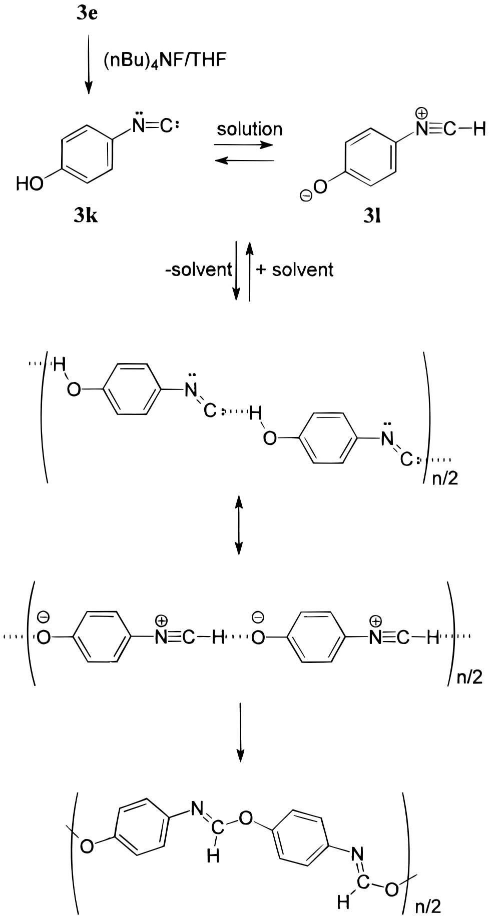


Figure 1. Plot of the ^{13}C isocyanide chemical shift, $\Delta\delta = (\delta C^o_X - \delta C^o_H)$, vs the Hammett σ parameter. The solid circles are the data for eight different substituent groups in the 4-position, the open circles are the values derived for the two uncommon substituent groups (**3e**, **3f**), and the triangles show the range of σ values for the H-bonded 4-hydroxyphenyl isocyanide example (**3k**, **3l**). The straight line is the least squares fit to the values from the eight common substituent groups (r^2 = 0.97).

stituents examined in this study and elsewhere.[13] An excellent linear relationship ($r^2 = 0.97$) was found for all the common substituent examples prepared but one (**3k**). The two uncommon substituent examples (**3e** and **3f**) that we have prepared generate Hammett σ constant values of −0.02 and −0.31, respectively. These generated σ values are logically consistent with the idea that these two substituents are weak (*N*-pyrrolo-) and moderate (OTBDMS) electron donors.

The only common substituent we have examined that did not fit nicely on the LFER correlation exhibited in Figure 1 was the *p*-hydroxy group. The Hammett σ constant for OH is reported to be[12] −0.37, which would put the observed chemical shift well above the best fit line (shown as the open triangle above the dashed line). Observation of this exception led us to the conclusion that a *p*-hydroxy anion group (**3l**) was partially in control of the chemical shift value at C° in *p*-hydroxyphenyl isocyanide (**3k**). This conclusion was supported by speculation in the literature[14] that the negatively charged phenoxy moiety is one of the most powerful electron donors available. It is difficult to determine a reliable Hammett σ constant for this negatively charged group because of the strong solute−solvent interactions that are present, but the range of reported values seems to coalesce around −0.6 to −1.0, so we used an average of −0.81 (*vide infra*) and plotted this as the lower filled triangle. If an equilibrium was present that involved both **3k** and **3l** (see Scheme 2), then the observed chemical shift value should have occurred along the dashed line in Figure 1, assuming a fast enough rate. This dashed line crossed the LFER correlation line at a point very close to the value displayed for **3j**, which seems logical if the proposed explanation is operative.

Scheme 2



The preparation of **3k** by desilylation of **3e** yielded an unstable compound which turned dark rapidly unless it was pure. The IR spectrum of the neat liquid, **3k**, exhibited a sharp band at 2124 cm^{-1} accompanied by a less intense band to the high energy side at ~2150 cm^{-1}.[15] Dissolution of **3k** in $CDCl_3$ indicated that this compound was fairly stable and maintained its integrity during the course of the NMR experiment. In the neat state, prior to chromatographic purification, **3k** was rather unstable and it decomposed rapidly at room temperature in a matter of hours. Purification produced a liquid that

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(14) Topsom, R. D. *Prog. Phys. Org. Chem.* **1987**, *16*, 125.

(15) This less intense, high-energy shoulder may be due to a Fermi resonance, as implied in ref 9. We did not pursue this explanation further as **3k** was the only example that showed this phenomenon. Another explanation might be that the shoulder could be associated with the proposed equilibrium that involved structure **3l**.

exhibited a reasonable elemental analysis. The compound **3k** did polymerize slowly, however, when dissolved in apolar solvent for extended periods of time.

As illustrated in Scheme 2, we believe that **3k**, when dissolved in a solvent, is probably involved in an equilibrium with **3l**. In the neat state this system is likely to have an extensive intermolecular hydrogen bonding network that connects **3k** to **3l**. It is not surprising, then, that this molecular system polymerized when dissolved in $CHCl_3$ for 2 weeks or more *via* an uncatalyzed, H-bond-assisted process, as shown in Scheme 2. The origin of this general type of reactivity has been described fully.[11] Scheme 2 nicely accommodates the end points of the processes involved.

The historical description of isocyanophenols is limited. The ortho-substituted example, 2-isocyanophenol, was first prepared and studied in 1973,[16] and it was shown by the authors that 2-isocyanophenol was readily converted to benzoxazole in a thermal process at room temperature. In 1983[17] it was observed that deprotonation of benzoxazole led to the *o*-isocyanophenoxide ion, which could be trapped using trimethylsilyl chloride. The acid dissociation constant of benzoxazole has been measured[18] ($pK_a < 15.7$). In 1995[9], the preparation of 4-isocyanophenol (**3k**) was reported, but little concerning the reactivity of this compound was described other than the implication that the corresponding phenoxide ion had been identified in DMSO solvent. These authors[9] reported that **3k** exhibited a solvent dependent IR band, ascribed to the isocyano group, that ranged from 2122 cm^{-1} in CCl_4 to 2129 cm^{-1} in $CHCl_3$, while the **3l** anion was assigned an isocyano IR stretch at 2118 cm^{-1} in DMSO. Further, the authors of this study[9] attempted to correlate "infrared frequencies and intensities" of the isocyano group with Hammett σ constants in 15 meta- and para-substituted phenyl isocyanide examples, but their results could not "...be explained simply within the LFER approach". Despite these difficulties, the authors did assign a value of $\sigma = -0.81$ for the *p*-oxide anion substituent. This seems reasonable to us in light of our explanation that an equilibrium is probably present in nonpolar solvent, which is probably unlike the situation in the polar solvent DMSO.

Dissolution of **3k** in $CHCl_3$ led to an uncatalyzed polymerization when dilute solutions were stirred at room temperature for extended periods of time. The black polymer that was produced had a chromatographic (GPC) molecular weight of about 5800 with a high polydispersity (the GPC band was very broad). This crude polymer exhibited an IR peak at 1670 cm^{-1}, assigned to an imine, and a very small band at 2124 cm^{-1}, associated with the remaining isocyano monomer (partial purification removed the 2124 cm^{-1} band). The IR spectrum of this new polymer was very different from the polymer prepared by catalytic polymerization of **3k** using Ni(II) ion[3], which exhibited an imine stretch at 1604 cm^{-1} in the IR spectrum. Confirmation that this newly prepared polymer was unlike the majority of polymers prepared catalytically from isocyanide compounds[4] was provided by the ^1H NMR spectrum. The monomer, **3k**, exhibited two doublets at 6.8 and 7.25 ppm and no observable OH resonance in $CDCl_3$.[19] The polymer produced by the Ni(II) catalyzed polymerization of **3k** exhibited a very broad ^1H NMR spectrum having only two resonance manifolds centered at 6.5 and 9.3 ppm in the ratio of 4:1, respectively. The unique polymer produced by the uncatalyzed polymerization of **3k** had a ^1H NMR spectrum with three broad resonance manifolds centered at 6.6, 7.2, and 9.2 ppm in an approximate ratio of 2:2:1, respectively. This information was consistent with the conclusion that the Ni(II)-catalyzed process yielded a normal poly(iminomethylene) type structure,[4] while the uncatalyzed process seemed to give a unique poly(iminoformate) type structure *via* an α-addition process,[11] as illustrated in Scheme 2. Obviously, further work will be required to characterize this unique polymer type and confirm that the structure is a poly(iminoformate ester). The polymeric structure shown in Scheme 2 is, however, compatible with the known chemistry of isocyanide compounds,[11] the analogous properties of *o*-hydroxyphenyl isocyanide,[16-18] and the spectral information thus far gathered experimentally.

In conclusion, we have shown that the isocyano group can be used as an easily accessible probe to develop an LFER correlation of the Hammett type. Additionally, we have utilized an LFER analysis to point the way to the development of some unique polymer chemistry. Lastly, we have found that the isocyano group can apparently participate in an interesting type of intermolecular hydrogen bonding network with a *p*-hydroxy group of a phenyl ring.

Experimental Section

IR spectra were recorded on a Perkin-Elmer 1650 series FTIR spectrometer as KBr pellets or as neat liquids between salt plates in the range 4000−400 cm^{-1}. ^1H and ^{13}C NMR spectra were obtained on a Bruker AM300 spectrometer in $CDCl_3$ solution at 300 MHz for ^1H and 75 MHz for ^{13}C. Chemical shifts are referenced downfield from TMS. UV−vis spectra were obtained on a Perkin-Elmer $\lambda 2$ spectrometer in acetonitrile solutions. Gel permeation chromatography experiments were carried out on a Perkin-Elmer 1020 LC computer-controlled chromatographic system using a Perkin-Elmer binary LC 250 pump and a Perkin-Elmer UV-VIS LC 290 spectrophotometric detector and using 10^3 and 10^4 Å Ultrastyragel columns. Melting points were determined using a Mel-Temp capillary melting point apparatus and are reported uncorrected. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. All chemicals used were commercially available reagent grade with the exception of the known acetic formic anhydride, which was prepared from published procedures.[7] All starting materials were checked for purity by melting point, boiling point, and/or IR and NMR spectroscopy. Solids were recrystallized and liquids distilled where necessary. All of the monomeric isocyanides have a sickening stench and must be handled only in a well-functioning hood. Most of the *p*-substituted phenyl isocyanides have been prepared previously as described in the literature.[6]

***N*-Formyl-4-hydroxyaniline (2k).** Acetic formic anhydride[7] (3.9 g, 44 mmol) was added slowly to a stirred solution of *p*-aminophenol (3.0 g, 27.5 mmol) in tetrahydrofuran (80 mL) and held at 0 °C in an ice bath. The reaction mixture was stirred as it warmed to room temperature and stirring was continued for 16 h. TLC analysis of the reaction mixture (80% ethyl acetate in hexane) showed complete disappearance of the starting amine and appearance of a new spot. Removal of the solvent by rotary evaporation followed by column chromatography (60% ethyl acetate in hexane) afforded the desired *N*-formyl-4-hydroxyaniline. Recrystallization from ethyl alcohol and benzene gave a

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[16] Ferris, J. P.; Antonucci, F. R.; Trimmer, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 919.

[17] Jutzi, P.; Gilge, U. *J. Organomet. Chem.* **1983**, *246*, 159.

[18] Fraser, R. R.; Mansour, T. S.; Savard, S. *Can. J. Chem.* **1985**, *63*, 3505.

[19] Our inability to observe the OH resonance implied that the equilibrium described in Scheme 2 is slow on the ^1H NMR time scale.

[20] LaPlanche, L. A.; Rogers, M. T. *J. Am. Chem. Soc.* **1964**, *86*, 337.

pure product (3.2 g, 84% yield): mp 138−140 °C; TLC $R_f = 0.38$ (80% ethyl acetate in hexane); IR (KBr) 3312, 3096, 1664, 1561, 1510, 1404, 1383, 1255, 1171, 1108, 830 cm^{-1}; syn isomer ^{1}H NMR (DMSO-d_6) δ 6.70 (d, 2H, J = 8.83 Hz), 7.37 (d, 2H, J = 8.80 Hz), 8.15 (d, 1H, J = 1.88 Hz), 9.26 (s, 1H); ^{13}C NMR δ 115.1, 120.8, 129.9, 153.5, 158.7; UV−vis (acetonitrile) $\lambda_{\max}$ 248 nm, $\epsilon = 2.1 \times 10^4$ anti isomer ^{1}H NMR (DMSO-d_6) δ 6.70 (d, 2H, J = 8.83 Hz), 6.98 (d, 2H, J = 8.71 Hz), 8.50 (d, 1H, J = 11.2 Hz), 9.85 (d, 1H, J = 11.5 Hz); ^{13}C NMR δ 115.7, 120.2, 129.6, 154.2, 162.4. The two isomers are in a 3:1 (syn:anti) ratio, and assignments were based on the intensities of the NMR peaks.[20]

***N*-Formyl-4-(*tert*-butyldimethylsiloxy)aniline (2e).** To a stirred mixture of *N*-formyl-4-hydroxyaniline (1.2 g, 11.1 mmol) in THF (50 mL) were added *tert*-butyldimethylsilyl chloride (2.0 g, 13.3 mmol) and triethylamine (1.9 mL, 13.3 mmol), and the mixture was held at 0 °C in an ice bath. The reaction mixture was stirred under a nitrogen atmosphere while it warmed to room temperature and stirring was continued overnight. TLC analysis (70% ethyl acetate in hexane) showed complete disappearance of the starting phenol and the appearance of a new spot. Removal of the solvent by rotary evaporation, followed by column chromatography (50% ethyl acetate in hexane), afforded the desired *N*-formyl-4-(*tert*-butyldimethylsiloxy)aniline as a colorless oil (2.6 g, 93% yield): TLC $R_f = 0.43$ (70% ethyl acetate in hexane); IR (neat) 3278, 3122, 3056, 2945, 2856, 1678, 1600, 1511, 1472, 1406, 1250, 1167, 911, 833, 778 cm^{-1}; syn isomer ^{1}H NMR (CDCl$_3$) δ 0.18 (d, 6H, J = 4.0 Hz), 0.98 (d, 9H, J = 2.3 Hz), 6.78−6.83 (t, 1H), 7.40 (d, 2H, J = 6.7 Hz), 7.53 (s, 1H), 8.30 (d, 1H, J = 1.9 Hz), 8.38 (s, 1H); anti isomer ^{1}H NMR (CDCl$_3$) δ 0.17 (d, 6H J = 4.0 Hz), 0.97 (d, 9H, J = 2.3 Hz), 6.78−6.83 (d, 1H), 6.98 (d, 1H, J = 6.6 Hz), 7.53 (br, 1H), 8.15 (d, 2H, J = 11.0 Hz), 8.53 (d, 2H, J = 11.5 Hz); ^{13}C NMR δ 115.7, 120.2, 129.6, 154.2, 162.4; (syn and anti) ^{13}C NMR δ −4.5, 18.2, 25.6, 120.4, 121.0, 121.4, 130.1, 130.5, 152.8, 153.7, 158.7, 162.9. The two isomers are in a 1:1 ratio and could be distinguished in the ^{1}H spectrum using saturation transfer techniques.

4-(*tert*-Butyldimethylsiloxy)phenyl Isocyanide (3e). To a stirred solution of *N*-formyl-4-(*tert*-butyldimethylsiloxy)aniline (2.1 g, 8.0 mmol) in dichloromethane (50 mL) were added the components triethylamine (1.2 g, 12 mmol), carbon tetrachloride (1.8 g, 12 mmol), and triphenylphosphine (3.1 g, 12 mmol), and the mixture was held at 0 °C in an ice bath. The reaction mixture was stirred under a nitrogen atmosphere while it warmed to room temperature and stirring was continued for 5 h. TLC analysis (70% ethyl acetate in hexane) showed complete disappearance of the starting formamide and the appearance of a new spot. Removal of the solvent by rotary evaporation followed by column chromatography (40% ethyl acetate in hexane) afforded the desired 4-(*tert*-butyldimethylsiloxy)phenyl isocyanide as a colorless oil (1.6 g, 83% yield): TLC $R_f = 0.48$ (70% ethyl acetate in hexane); IR (neat) 2956, 2123, 1602, 1504, 1472, 1272, 909, 839, 778 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.21 (s, 6H), 0.98 (s, 9H), 6.81 (dd, 2H, J = 6.7 and 6.7 Hz), 7.27 (d, 2H, J = 7.3 Hz); ^{13}C NMR δ −4.5, 18.2, 25.6, 120.0, 120.7, 127.7, 156.5, 163.2. Anal. Calcd: C, 66.95; H, 8.15; N, 6.00. Found: C, 66.75; H, 7.96; N, 5.85.

4-Hydroxyphenyl Isocyanide (3k). Tetrabutylammonium fluoride (1.2 mL, 1.2 mmol) was added slowly to a stirred solution of 4-(*tert*-butyldimethylsiloxy)phenyl isocyanide (0.23 g, 1.0 mmol) in THF (5.0 mL) and held at 0 °C in an ice bath. The reaction mixture was stirred under a nitrogen atmosphere for 15 min. TLC analysis (30% ethyl acetate in hexane) showed complete disappearance of the starting silyl ether and the appearance of a new spot. Removal of the solvent by rotary evaporation followed by column chromatography (20% ethyl acetate in hexane) afforded the desired 4-hydroxyphenyl isocyanide as a colorless oil (0.12 g, 97% yield): TLC $R_f = 0.42$ (30% ethyl acetate in hexane); IR (neat) 3278, 2124, 1610, 1594, 1508, 1448, 1369, 1280, 1225, 1189, 1161, 1102, 1066, 967, 928, 839 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.84 (d, 2H, J = 8.8 Hz), 7.25 (d, 2H, J = 8.7 Hz); ^{13}C NMR δ 116.5, 119.4, 128.2, 156.9, 161.5. Anal. Calcd: C, 70.60, H, 4.20; N, 11.80. Found: C, 69.96; H, 4.75; N, 11.36 (the elemental analysis is slightly off due to oxidation during the delay caused by transportation).

Poly((4-hydroxyphenyl)iminomethylene). To a stirred solution of anhydrous NiCl$_2$ (3.0 mg) in methyl alcohol (5.0 mL) was added 4-hydroxyphenyl isocyanide (0.22 g, 1.8 mmol) slowly. The reaction mixture was stirred at room temperature for 7 days. The polymerization was followed by observing the disappearance of the isocyanide by TLC and in the IR spectrum of the reaction mixture. The precipitates were isolated by suction filtration. After washing thoroughly with methyl alcohol, the resulting polymer, poly((4-hydroxyphenyl)iminomethylene), was dried *in vacuo* to give a black solid (165 mg, 75% yield): mp 340−342 °C (dec); IR (KBr) 3411, 1604, 1500, 1439, 1361, 1228, 1150, 1094, 1006, 828 cm^{-1}; UV−vis (dichloromethane) $\lambda_{\max}$ 416 nm; ^{1}H NMR (DMSO-d_6) δ 6.5 (br, 4H), 9.3 (br, 1H).

Poly(iminomethyleneoxy-1,4-phenylene). 4-Hydroxyphenyl isocyanide (0.36 g, 3.0 mmol) was added slowly to chloroform (5 mL) and the reaction mixture was stirred at room temperature for 14 days. The polymerization was followed by observing the disappearance of the isocyanide by TLC and in the IR spectrum of the reaction mixture. The precipitates were isolated by suction filtration. After washing thoroughly with chloroform, the resulting polymer, $=(\mathrm{CHO}\text{-}\varphi\text{-}\mathrm{N}{=}\mathrm{CHO}\text{-}\varphi\text{-}\mathrm{N})_n=$, was dried *in vacuo* to give a black solid (230 mg, 63% yield). This black solid could be partially purified in the following manner: dissolution in glyme yields a deep red solution which can easily be filtered to remove some black, gummy material. Reprecipitation with hexane separates a dark solid which can be washed with ethyl acetate until the washings are no longer yellow. Any trapped ethyl acetate can be removed from this powdery dark solid by washing with hexane. Spectral analysis clearly indicates that this powder is not a single material: mp 260−269 °C (dec); IR (KBr) 3379, 2948, 1670, 1617, 1513, 1457, 1384, 1226, 833, cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 6.6 (br, 2.6H), 7.2 (br, 2.1H), 9.1 (br, 1.0H) (the first two broad resonances overlap).

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