

Structural insights into Lewis acid- and F4TCNQ-doped conjugated polymers by solid-state magnetic resonance spectroscopy

Alana L. Dixon,^a Hervé Vezin,^b Thuc-Quyen Nguyen*^a and G. N. Manjunatha Reddy*^c

^a Center for Polymers and Organic Solids, University of California Santa Barbara (UCSB)
Santa Barbara, California 93106, USA
E-mail: guyen@chem.ucsb.edu

^b University of Lille, CNRS UMR8516, LASIRE, F-59000, Lille, France

^c University of Lille, CNRS, Centrale Lille Institut, Univ. Artois, UMR 8181–UCCS– Unité de Catalyse et Chimie du Solide, F-59000, Lille, France
E-mail: gnm.reddy@univ-lille.fr

Table of Contents

1. Experimental details
2. ¹H MAS NMR spectra of neat P4, P4:BCF and P4:F4TCNQ blends
3. ¹H→¹³C CP-MAS spectra of neat P4, P4:BCF and P4:F4TCNQ blends
4. Lineshape fitting analysis of ¹H MAS NMR spectra
5. 2D ¹H-¹³C heteronuclear correlation (HETCOR) spectrum of P4 polymer
6. 2D ¹H-¹H DQ-SQ correlation NMR spectrum of P4 polymer
7. 2D ¹H-¹H DQ-SQ NMR spectra of P4:BCF and P4:F4TCNQ blends
8. 2D ¹H-¹H DQ-SQ NMR spectra of P4, P4:BCF and P4:F4TCNQ blends
9. EPR spectra of pristine P4, P4:F4TCNQ, P4:BCF and P4:BCF-water blends
10. Longitudinal relaxation time (*T*₁) measurements and analysis
11. 2D ¹⁹F-¹⁹F spin diffusion NMR spectra of P4:F4TCNQ blends
12. References

1. Experimental details

Materials and synthesis. The polymer poly[2,6-(4,4-bis(2-hexadecyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7(2,1,3-benzothiadiazole)] (P4) was purchased from 1-Material, tris(pentafluorophenyl)borane (BCF) was purchased from TCI America and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) was purchased from Lumtec, and all were stored in a nitrogen glovebox and used as received. Stock solutions of the dopants (10 mg/ml BCF, 0.2 mg/ml F4TCNQ in chloroform) were prepared and then added in the proper ratio to solutions of P4 which was also dissolved in chloroform. The solutions of the doped polymer were allowed to sit overnight before being sealed under nitrogen in an airtight sample holder for drying via rotary evaporation at room temperature. The rotary evaporator was purged 3 times with nitrogen before opening the valve connecting the sample to the vacuum of the rotary evaporator. Once dry, the sample holder was filled with nitrogen again before being brought into the glovebox where the material was scraped into clean vials prior to the ssNMR measurements.

Solid-state NMR spectroscopy. Pristine P4, P4:BCF (1:0.05, 1:0.2, and 1:1 molar ratios) and P4:F4TCNQ (1:0.02 and 1:0.2 molar ratios) were separately packed into either 1.3 mm (outer diameter) or 3.2 mm (outer diameter) cylindrical zirconia rotors and fitted with Vespel® caps. All fast MAS (50 KHz) 1D ^1H , ^{19}F , and 2D ^1H - ^1H and ^{19}F - ^{19}F NMR experiments were carried out on a Bruker AVANCE NEO (18.8 T, Larmor frequencies of ^1H , ^{13}C , ^{11}B and ^{19}F were 800.1 MHz, 201.2 MHz, 256.7 MHz and 752.8 MHz respectively) spectrometer with 1.3 mm H-X probehead unless otherwise stated. The ^1H and ^{13}C experimental shifts were calibrated with respect to neat TMS using adamantane as an external reference (higher ppm ^{13}C resonance, 35.8 ppm, and the ^1H resonance, 1.85 ppm), and ^{19}F chemical shifts were calibrated to the ^{19}F chemical shift of Teflon at -132 ppm, in turn calibrated using neat CFCl_3 (^{19}F , 0 ppm) as an external reference. The ^{11}B MAS NMR spectra are referenced using an external standard NaBH_4 (^{11}B peak at -42.06 ppm), which is calibrated to $\text{BF}_3\cdot\text{OEt}_2$ (^{11}B , 0 ppm) in CDCl_3 .

1D MAS NMR experiments. For all materials, single-pulse ^1H MAS NMR experiments were carried out by co-adding 32 transients. ^1H relaxation delays were of 3 s and 2 s for the pristine P4 polymer and P4:dopant blends, respectively. In all cases, the ^1H and ^{19}F T_1 relaxation delays were measured by saturation recovery experiments and analysis. All 1D ^1H → ^{13}C cross polarization (CP)-MAS experiments of neat materials and blends were carried out at Bruker 9.4 T spectrometer (Larmor frequencies were ^1H = 400 MHz, and ^{13}C = 100.6 MHz). ^1H → ^{13}C CP-MAS spectra of P4, P4:BCF (1:1) and P4:F4TCNQ (1:0.2) were acquired by co-adding 4096, 16384, 20480 transients, respectively, with a CP contact time of 4 ms. Heteronuclear decoupling was applied during the acquisition period using two-pulse phase modulation (TPPM) decoupling sequence.¹ For F4TCNQ and P4:F4TCNQ blends, 1D ^{19}F MAS experiments were acquired using a spin echo sequence with an echo delay corresponding to one rotor period. For pristine BCF and P4:BCF blends, 1D ^{11}B MAS experiments were carried out at 18.8 T with 20 kHz MAS using a spin echo sequence with an echo delay corresponding to one rotor period. For P4:BCF+water and P4:BCF+D₂O titration experiments, ~20 μl of Millipore water or D₂O was added to 9 mg of blend materials and allowed to set at room temperature. 1D ^1H and ^{11}B MAS NMR experiments of these materials were separately carried out for P4:BCF+water and P4:BCF+D₂O blends.

1D lineshape analysis. ^1H lineshape analysis was carried out using Bruker Topspin (sola) package. For neat P4 and P4:dopant blends and P4:BCF+water blends, the ^1H signals corresponding to aliphatic, water and aromatic sites were deconvoluted in order to estimate the peak integrals, which are compared in Table S1.

2D MAS NMR experiments. 2D ^1H - ^1H DQ-SQ correlation spectra were acquired using a one rotor period Back-to-Back (BaBa) sequence at fast MAS.²⁻⁴ All 2D ^1H - ^1H DQ-SQ spectra of neat P4 material,

P4:F4TCNQ and P4:BCF blends were acquired using 128 t_1 increments, each by co-adding 16 transients with a rotor-synchronized t_1 increment of 20 μs . 2D ^1H - ^{13}C heteronuclear correlation (HETCOR) spectrum of pristine P4 was acquired with 128 t_1 increments, each with 16 co-added transients, to construct the indirect ^{13}C dimension using STATES-TPPI method. 2D ^{19}F - ^{19}F spin-diffusion experiments were carried out using a three-pulse NOESY-like sequence,⁵⁻⁷ with 80 t_1 increments, each by co-adding 16 transients with a rotor-synchronized t_1 incremental period of 20 μs .

Solid-state EPR spectroscopy. For all materials, 1D continuous-wave length (CW)-EPR spectra were acquired at X-Band using 0.1 mW microwave power and 0.5 G of amplitude modulation. Pulsed 2D hyperfine sublevel correlation spectroscopy (HYSCORE) experiments were performed at low temperature (4 K) using a four-pulse sequence $(\pi/2)-\tau-(\pi/2)-t_1-(\pi)-t_2-(\pi/2)$ -detection(echo) with pulse lengths of $\pi/2$ and π pulses of 28 ns and 52 ns, respectively. The delay $\tau = 300$ ns was chosen as an optimum to remove the strong FID signal due to homogenous part of EPR line and to prevent blind spot effects. The spectra were acquired with 256 \times 256 data points to accumulate t_1 and t_2 time domains. The unmodulated part of the echo was removed by second-order polynomial subtraction. Final HYSCORE spectra were obtained by 2D-Fourier transformation, using a Hamming apodization window function.

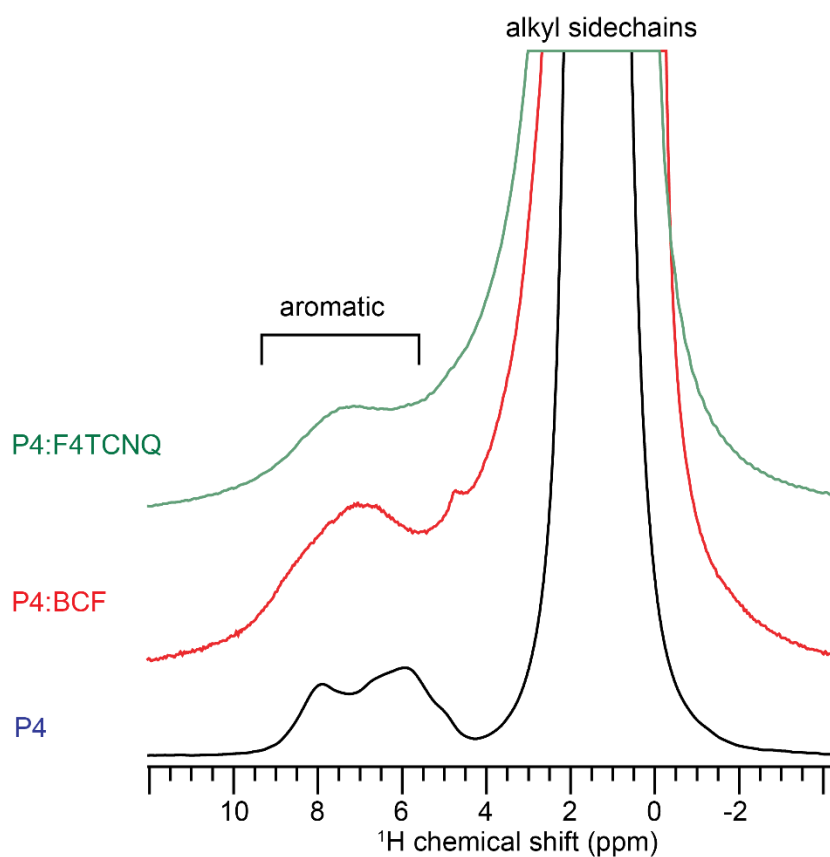
2. ^1H MAS NMR spectra of neat P4, P4:BCF and P4:F4TCNQ blends

Figure S1. Solid-state 1D ^1H MAS NMR spectra of pristine P4 and P4:BCF (1:1 molar ratio) and P4:F4TCNQ (1:0.2 molar ratio) blends show changes in the frequencies and lineshapes in the aromatic and aliphatic regions. All spectra were acquired at 18.8 T (^1H , 800.1 MHz) with 50 kHz MAS at room temperature.

3. $^1\text{H} \rightarrow ^{13}\text{C}$ CP-MAS spectra of neat P4, P4:BCF and P4:F₄TCNQ blends

Figure S2 compares $^{13}\text{C}\{^1\text{H}\}$ CP MAS NMR spectra of neat P4, P4:BCF and P4:F₄TCNQ blends. In a $^{13}\text{C}\{^1\text{H}\}$ CP MAS experiment, the ^1H and ^{13}C sites are simultaneously excited and $^1\text{H} \rightarrow ^{13}\text{C}$ polarization transfer is achieved to enhance the intensities of the latter. While the conventional $^{13}\text{C}\{^1\text{H}\}$ CP-MAS spectra do not provide quantitative information because ^{13}C signals are nonuniformly enhanced by the polarization transfer from neighboring ^1H sites, nonetheless, relative peak integrals of alkyl versus aromatic signals in neat P4, P4:BCF and P4:F₄TCNQ blends can be used to estimate the degree of line broadening and intensity losses associated with the aromatic and aliphatic regions. In P4, the ratio of alkyl/aromatic signal intensity is 1.0/0.53. By comparison, the ratio of alkyl/aromatic signal intensities in P4:BCF and P4:F₄TCNQ are 1.0/0.12 and 1.0/0.15, suggesting that the aromatic ^{13}C sites in the doped P4 polymers undergo greater signal intensity losses than the alkyl regions. Of particular note, aliphatic and aromatic sites of P4:dopant blends exhibit different degrees of intensity losses, as will be corroborated by the quantitative ^1H NMR analysis of neat P4 and P4-dopant blends discussed below.

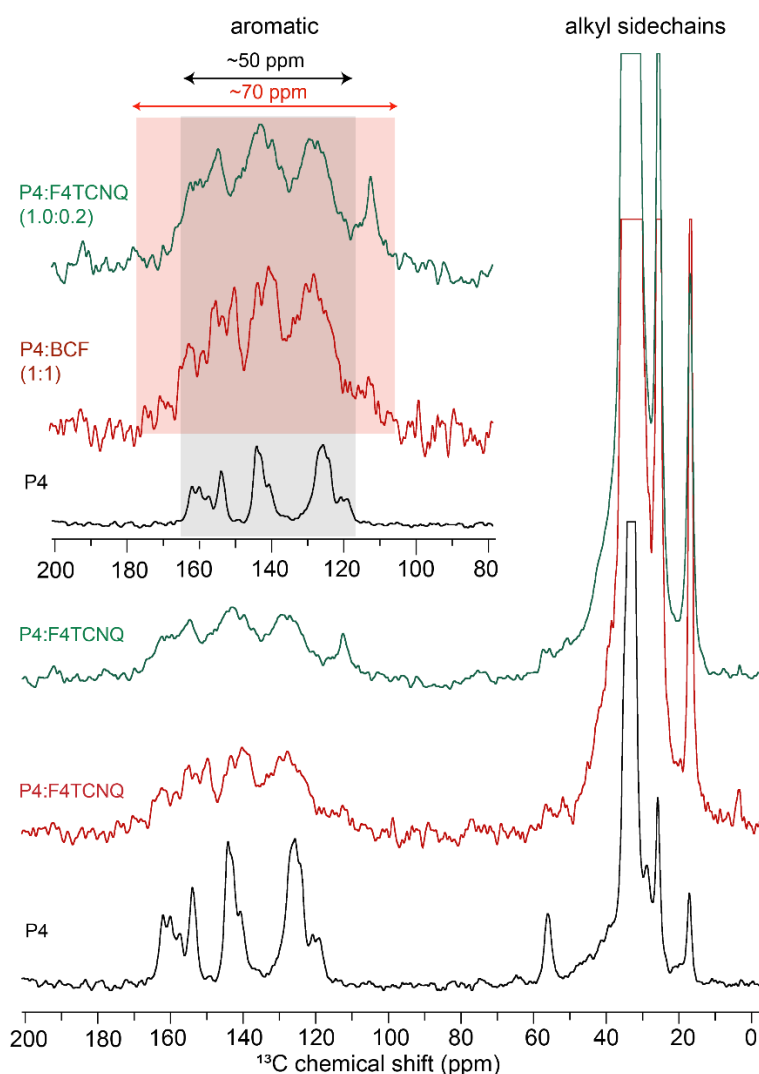


Figure S2. Solid-state 1D $^1\text{H} \rightarrow ^{13}\text{C}$ CP MAS NMR of neat P4, P4:BCF (1:1) and P4:F₄TCNQ (1:0.2) blends. Inset figure shows the expanded aromatic regions depicting the signal broadening in P4:dopant blends compared to the P4 polymer. All spectra were acquired at 9.4 T (^1H =400 MHz) and at room temperature with 4 ms CP contact time.

4. Lineshape fitting analysis of 1D ^1H MAS NMR spectra

For undoped and doped P4 polymers (~ 2.5 mg of each), ^1H MAS spectra were acquired at identical experimental condition, and the aliphatic/aromatic peak integrals were deconvoluted and compared (**Figure S3**). To convolute the lineshape of P4 ^1H spectrum (**Figure S3a**), we use the knowledge of the aromatic ^1H chemical shifts obtained from the analysis of 2D ^1H - ^{13}C and ^1H - ^1H correlation spectra (**Figures S4** and **S5**). Although deconvolution analysis does not provide information on the relative populations of different aromatic and aliphatic ^1H sites in doped polymers, nonetheless, it enables the aliphatic/aromatic signal integral ratio (66/4.7) in pristine P4 polymer to be estimated. In P4, the alkyl sidechains contain 66 hydrogen atoms and aromatic backbone contains 4 hydrogen atoms. By comparison, the peak integral of aliphatic signal in doped P4:F4TCNQ is ~ 36.3 , (calibrated with respect to 66 in neat P4) in P4:BCF ~ 49.5 , and P4:BCF+water is ~ 13.2 , suggesting the signal intensity loss in aliphatic regions. In a similar manner, ^1H signal intensity loss of aromatic groups is estimated for P4:dopant blends (**Table S1**). This analysis indicates that P4:F4TCNQ and P4:BCF blends exhibit different degrees of peak broadening and intensity loss, which can be attributable to different distributions of free radicals and doping mechanisms. With these factors in mind, we hypothesize that the detected ^1H signal intensities are expected to be largely originating from the diamagnetic regions of doped polymers, making it difficult to obtain an accurate quantitative analysis of signal intensity loss.

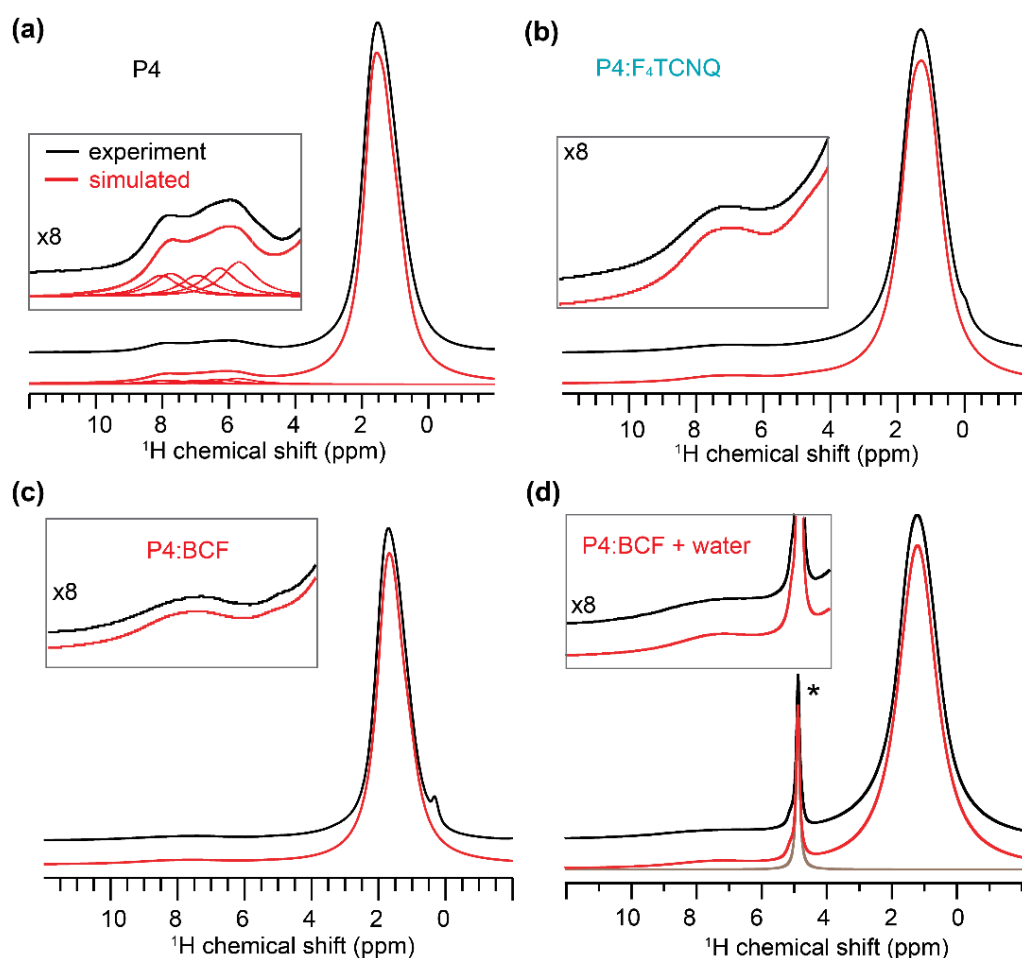


Figure S3. Lineshape analysis of 1D ^1H MAS NMR spectra of (a) pristine P4, (b) P4:F4TCNQ (1:0.2) (c) P4:BCF (1:1), and (d) P4:BCF (1:1) + water, indicating the different signal intensities, which are quantified and presented in **Table S1**. *denotes the signal from residual water.

Table S1. Alkyl and aromatic ^1H peak intensities in P4 polymer, and P4:BCF and P4:F4TCNQ blends

Material	^1H signal integral (a.u.)	
	Alkyl	Aromatic
P4	66.0	4.7
P4:F4TCNQ (1:0.2)	36.3	1.7
P4:BCF (1:1)	49.5	1.4
P4:BCF (1:1) + water	13.2	0.5

5. 2D ^1H - ^{13}C heteronuclear correlation (HETCOR) NMR spectrum of P4 polymer

In a 2D ^1H - ^{13}C HETCOR spectrum presented in **Figure S5**, different distributions of 2D peaks between 20-40 ppm (^{13}C) and 0-3 ppm (^1H) are due to the inter- and intramolecular dipolar coupled ^1H - ^{13}C moieties in alkyl sidechains. A 2D peak at ~ 53 ppm (^{13}C) and 1-3 ppm (^1H) is due to the through-space interactions between quaternary carbon atom and alkyl sidechain protons (cyan arrows) as depicted in the schematic structure. In the aromatic region, a peak at ~ 122 ppm (^{13}C) and 5.7-6.4 (^1H) ppm is attributable to hydrogenated carbon atoms (cyan dots) of BT groups, and a peak at 122-125 ppm (^{13}C) and 7.2-8.4 (^1H) ppm is attributable to hydrogenated carbon atoms (purple dots) and the alkyl sidechain protons indicates the close proximity between CPDT groups and thiophene carbon atoms (red arrows) as shown in the schematic structure. These peak assignments aid the analysis of ^1H DQ-SQ correlation spectra discussed in **Figure 2** (main text) and Figures S5-S7 discussed below, and provide a basis for the deconvolution analysis of the ^1H NMR spectrum presented in **Figure S3a**.

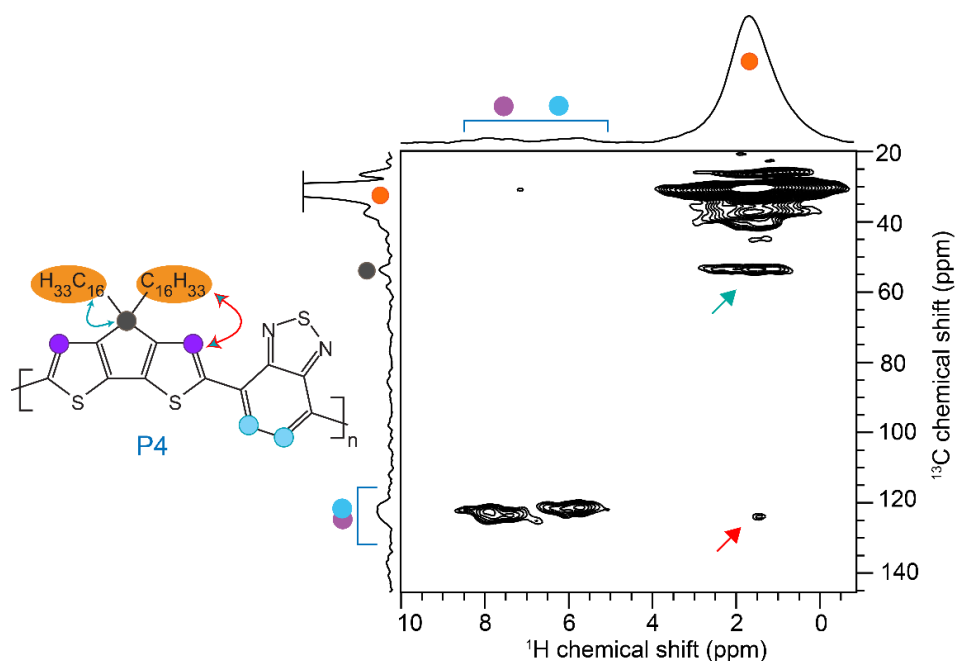


Figure S4. Solid-state 2D ^1H - ^{13}C heteronuclear correlation (HETCOR, ^1H -detected) spectrum of P4 acquired at 18.8 T (^1H , 800.1 MHz), 50 kHz MAS and at room temperature with 2 ms of CP contact time. The top horizontal and left vertical spectra are the summed projections of the ^1H and ^{13}C dimensions. 2D correlation peaks corresponding to aliphatic and aromatic moieties are color coded as depicted in the schematic structure. The cyan (^{13}C , ~ 53 ppm) and red (^{13}C , ~ 123 ppm) arrows indicate the through-space dipolar interactions between quaternary carbon atoms and alkyl sidechains (black dot), and between hydrogenated thiophene carbon atoms (purple dots) and alkyl sidechains.

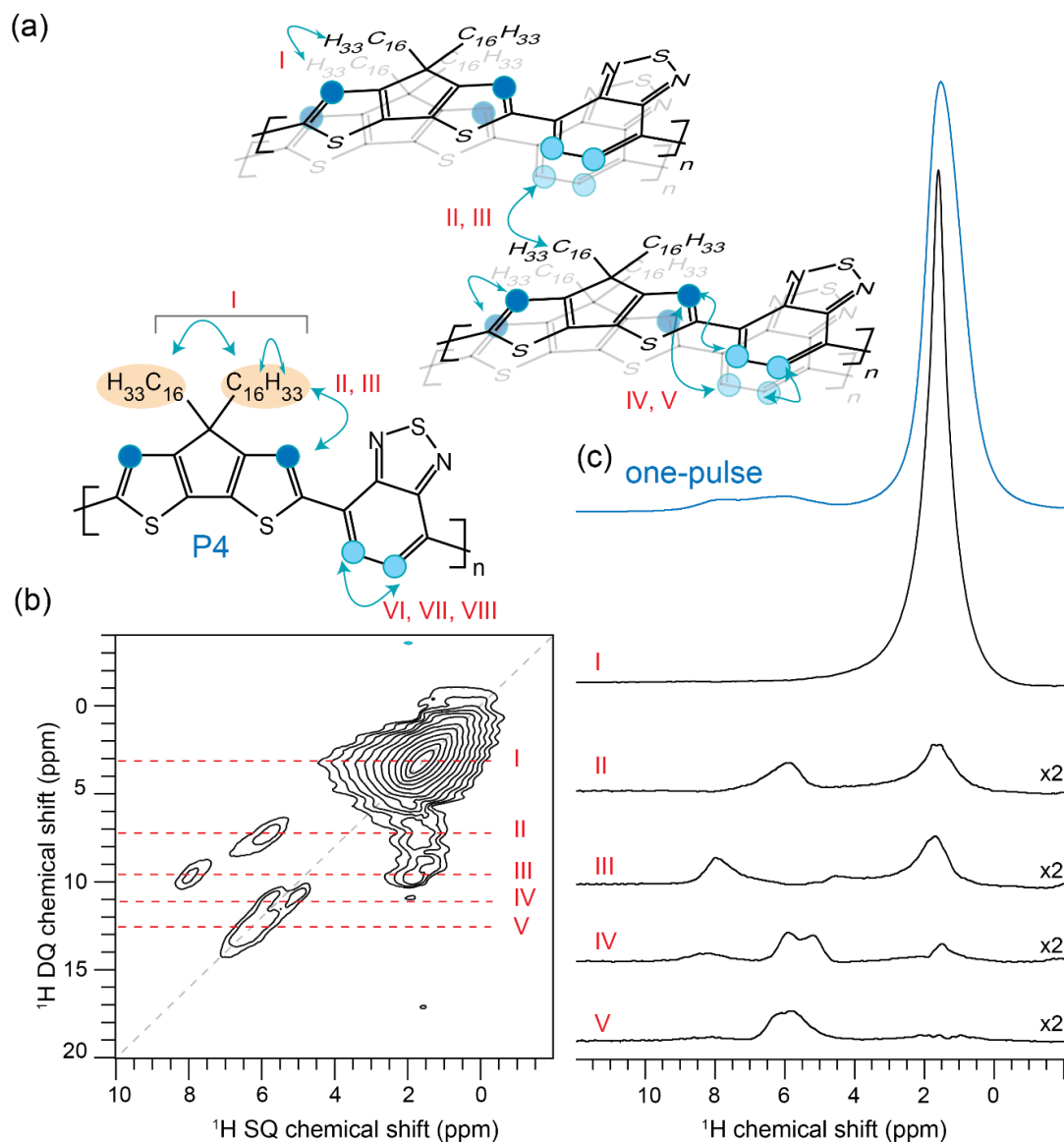
6. 2D ^1H - ^1H DQ-SQ correlation NMR spectrum of P4 polymer

Figure S5. (a) Molecular structure of P4 with through-space ^1H - ^1H dipolar interactions that may contribute to ^1H DQ signals. (b) Solid-state 2D ^1H - ^1H DQ-SQ correlation spectrum of pristine P4, together with (c) line-cut SQ spectra at specific DQ peaks correspond to the through-space interactions shown in (a). In (c), a single-pulse ^1H spectrum is shown for a comparison. All spectra were acquired at 18.8 T (^1H = 800.1 MHz), 50 kHz MAS and at room temperature.

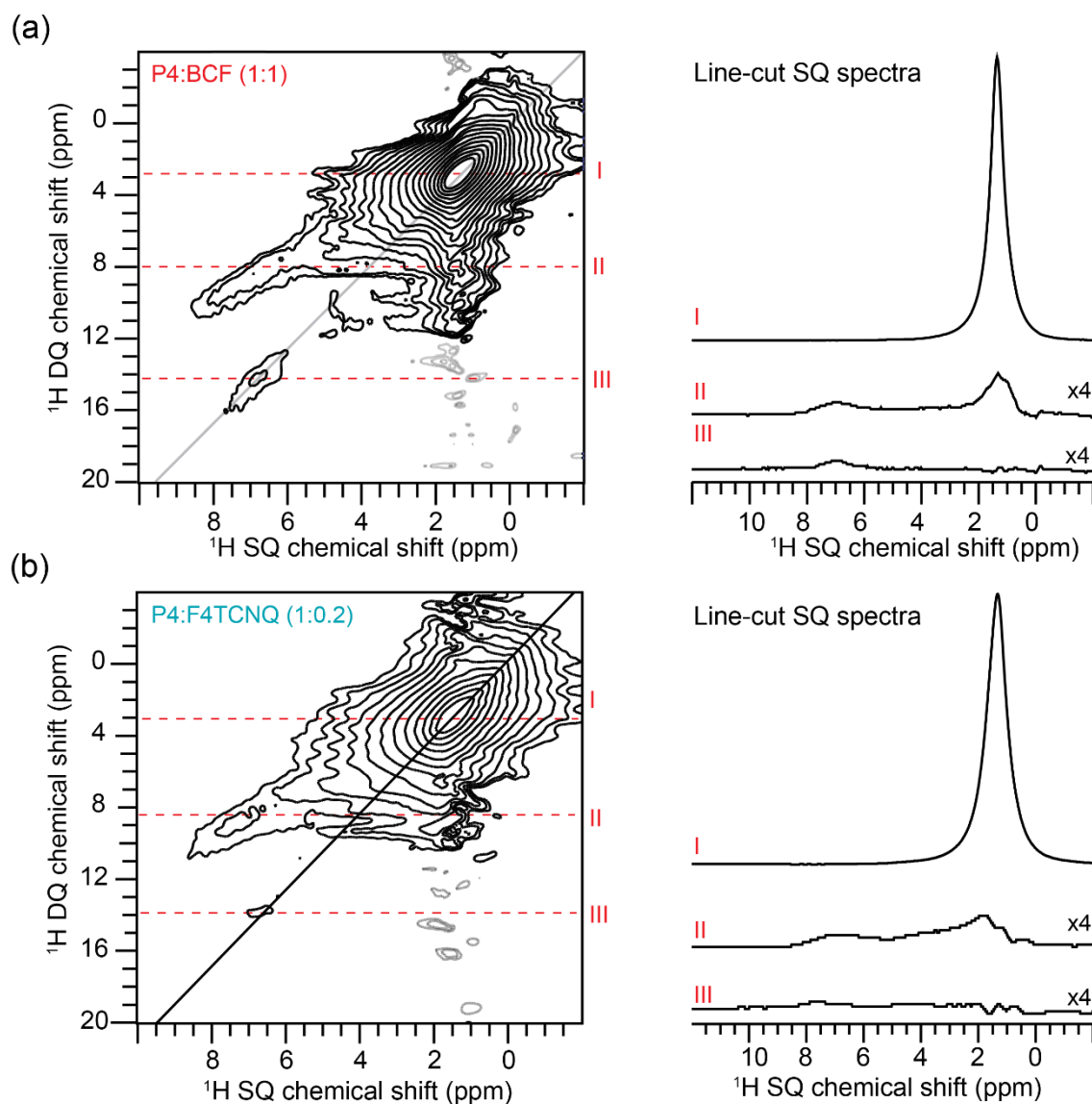
7. 2D ^1H - ^1H DQ-SQ NMR spectra of P4:BCF and P4:F4TCNQ blends

Figure S6. Solid-state 2D ^1H - ^1H DQ-SQ correlation NMR spectra of (a) P4:BCF and (b) P4:F4TCNQ doped polymers together with their line-cut SQ spectra at specific DQ chemical shifts that indicate the significant intensity losses for aromatic regions of P4 polymer. Weak intensity aromatic peaks (III) in the line-cut spectra are most likely due to artifacts or expected to originate from weak residual ^1H DQ signals of undoped polymer regions. This is consistent with the EPR analysis that showed the presence of F4TCNQ radicals (located at much closer proximities to P4 backbones) and BCF moieties (located in the vicinity of P4 backbones). All spectra were acquired at 18.8 T (^1H = 800.1 MHz) with 50 kHz MAS at room temperature.

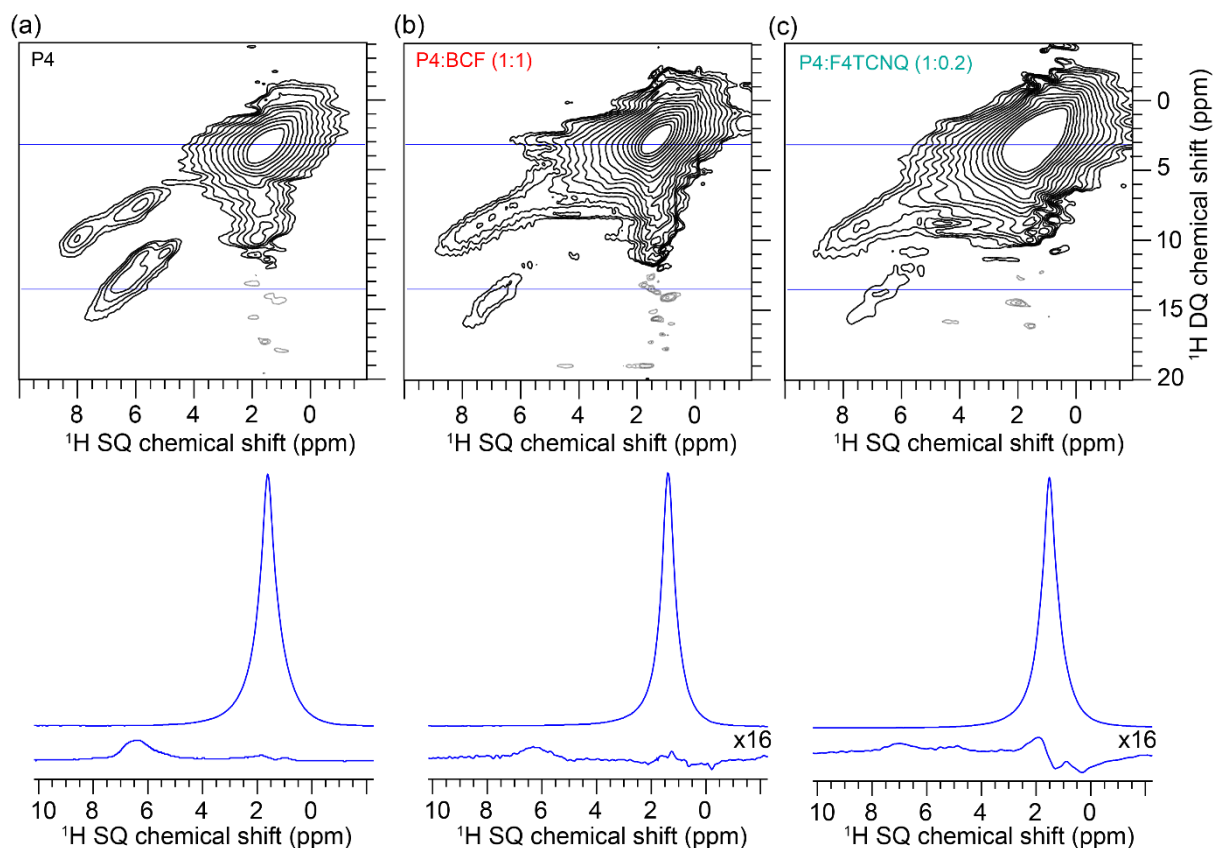
8. 2D ^1H - ^1H DQ-SQ NMR spectra of P4, P4:BCF and P4:F4TCNQ blends

Figure S7. Solid-state 2D ^1H - ^1H DQ-SQ correlation NMR spectra of (a) P4, (b) P4:BCF and (c) P4:F4TCNQ acquired with a longer recoupling time of 40 microseconds (corresponding to two rotor periods, $2\tau_r$ with 50 kHz MAS frequency). For each spectrum, line-cut SQ spectra extracted for the ^1H DQ peaks at 3.5 and 13.5 ppm (horizontal blue solid lines in a-c) are compared in the bottom panels. Although the 2D peaks are relatively better visible in the aromatic regions of doped P4 polymers, their signal intensities remain closer to the noise level, indicating that these signals are most likely artefacts or very weak residual DQ peaks originating from the diamagnetic regions of the doped P4 polymers. The base contours are at (a) 6%, (b) 0.6% and (c) \sim 0.8% of the maximum peak intensity.

9. EPR spectra of pristine P4, P4:F4TCNQ, P4:BCF and P4:BCF-water blends

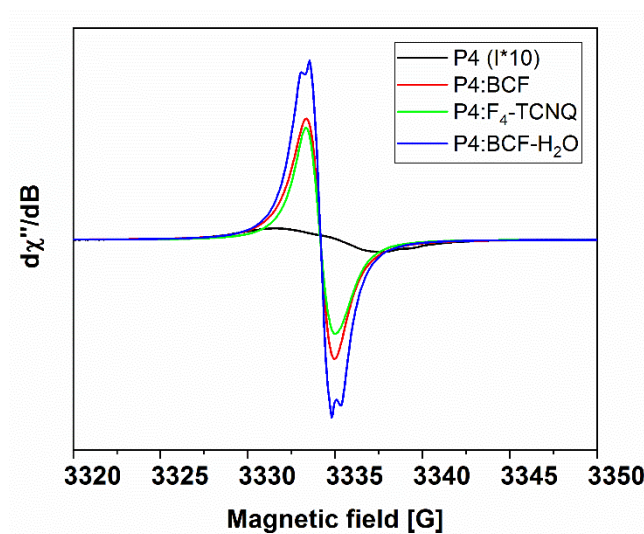


Figure S8. Solid-state X-band continuous-wave EPR spectra of P4, P4:F4TCNQ, P4:BCF and P4:BCF-water blends.

10. Longitudinal relaxation time (T_1) measurements and analysis

For pristine P4 polymer and P4:dopant blends, the longitudinal relaxation times (T_1) associated with aromatic and alkyl sidechain ^1H sites were measured using saturation recovery experiments at 18.8 T (50 kHz MAS). A pseudo-2D NMR experiment was acquired using a saturation recovery sequence. T_1 values were measured using Topspin package and compared (Table S2). For neat F4TCNQ, it was feasible to obtain a pseudo-2D NMR spectrum acquired as a function of saturation recovery delay. For P4:F4TCNQ (1:0.2), dilute concentration of dopant molecules and different distributions of ^{19}F signals originating from different locally disordered regions lead to poor signal-to-noise ratio. In addition, these signals are obscured by a background signal. Therefore, a T_2 -filter (i.e., a spin echo block with 1 rotor period) was added to suppress the background signal in order to identify the ^{19}F signals originating from the dopants. T_2 -filtered 1D ^{19}F spectra were acquired by varying an inter-scan repetition delay in the range between 0.5 s and 50 s (Figure 5, main text). T_1 values are given in Table S2.

Table S2. T_1 relaxation times of ^1H sites in P4, and P4:BCF and P4:F4TCNQ materials

Material	^1H T_1 relaxation time (s)	
	Alkyl chains	Aromatic
P4	0.93	0.98
P4:F4TCNQ (1:0.2)	0.16	0.03
P4:BCF (1:1)	0.87	0.89
P4:BCF (1:1) + water	0.57	#
Material	^{19}F T_1 relaxation time (s)	
F4TCNQ	378	
P4:F4TCNQ (1:0.2)	< 100	

signal intensity is too weak for the T_1 value to be determined.

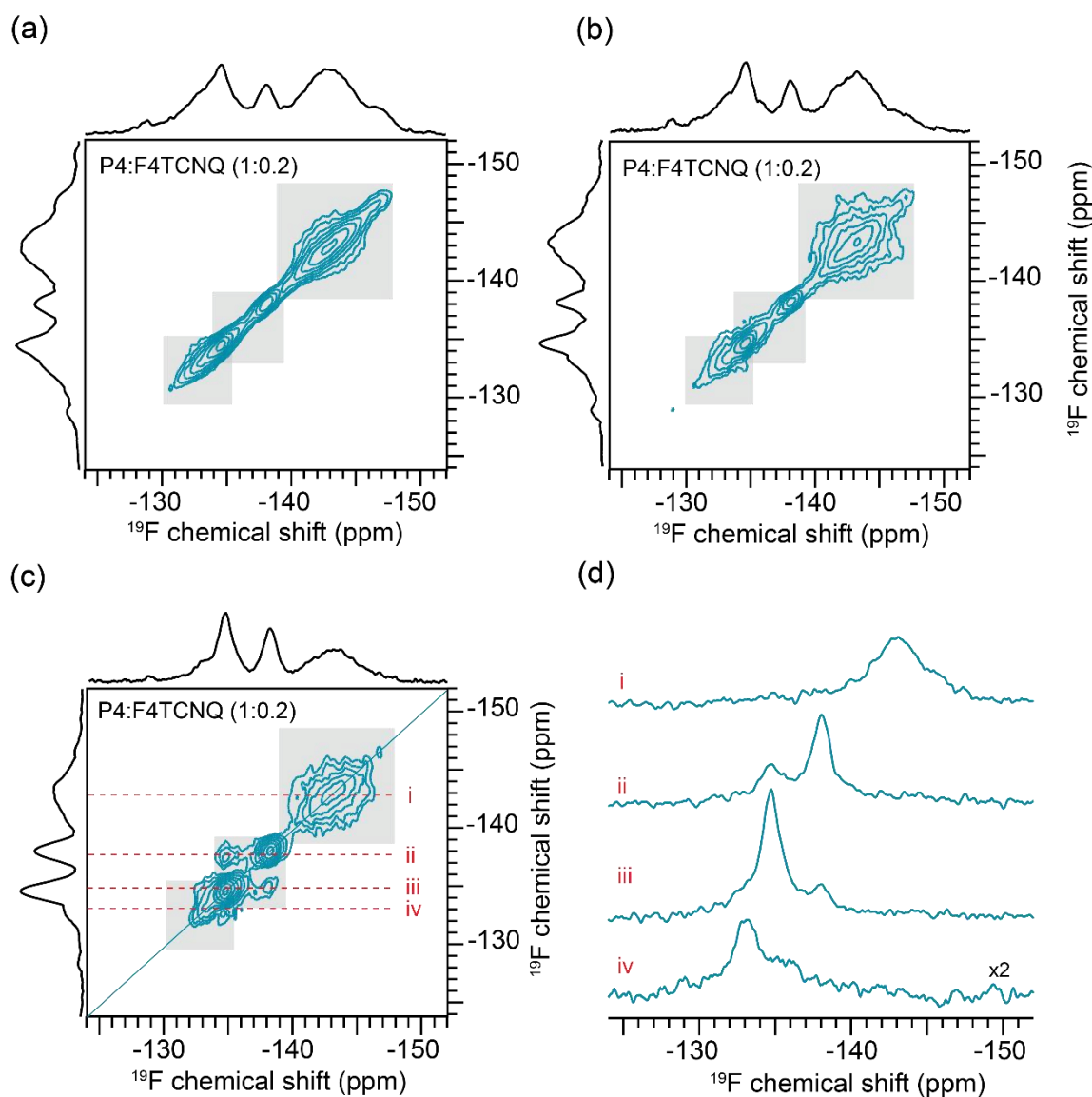
11. 2D ^{19}F - ^{19}F spin diffusion NMR spectra of P4:F4TCNQ blends

Figure S9. Solid-state 2D ^{19}F - ^{19}F spin-diffusion NMR spectra of P4:F4TCNQ acquired with (a) 10 ms (b) 100 ms and (c) 500 ms of mixing time. The signals correspond to locally ordered and disordered regions are depicted in gray boxes. The cross peaks did not appear in (a) and (b), whereas cross peaks are observed between ^{19}F sites in the ordered regions. (d) line-cut spectra extracted from (c) for different ^{19}F signals (i-iv). All spectra were acquired at 18.8 T (Larmor frequency of ^{19}F = 752.8 MHz) with 50 kHz MAS at room temperature.

12. References

- 1 A. Khitrin and B. M. Fung, *J. Chem. Phys.*, 2000, **112**, 2392–2398.
- 2 I. Schnell and W. H. Spiess, *J. Magn. Reson.*, 2001, **151**, 153–227.
- 3 G. N. Manjunatha Reddy, M. Malon, A. Marsh, Y. Nishiyama and S. P. Brown, *Anal. Chem.*, 2016, **88**, 11412–11419.
- 4 Y. lee Hong, G. N. Manjunatha Reddy and Y. Nishiyama, *Solid State Nucl. Magn. Reson.*, 2020, **106**, 101651.
- 5 G. N. M. Reddy, A. Huqi, D. Iuga, S. Sakurai, A. Marsh, J. T. Davis, S. Masiero and S. P. Brown, *Chem. - A Eur. J.*, 2017, **23**, 2235.
- 6 A. Karki, J. Vollbrecht, A. L. Dixon, N. Schopp, M. Schrock, G. N. M. Reddy and T. Nguyen, *Adv. Mater.*, 2019, **31**, 1903868.
- 7 A. Karki, J. Vollbrecht, A. J. Gillett, S. S. Xiao, Y. Yang, Z. Peng, N. Schopp, A. L. Dixon, S. Yoon, M. Schrock, H. Ade, G. N. M. Reddy, R. H. Friend and T. Q. Nguyen, *Energy Environ. Sci.*, 2020, **13**, 3679–3692.