

Influence of TiO₂ nanoparticles on liquid crystalline, structural and electrochemical properties of (8Z)-N-(4-((Z)-(4-pentylphenylimino)methyl)benzylidene)-4-pentylbenzenamine

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Synthesis of AZJ1

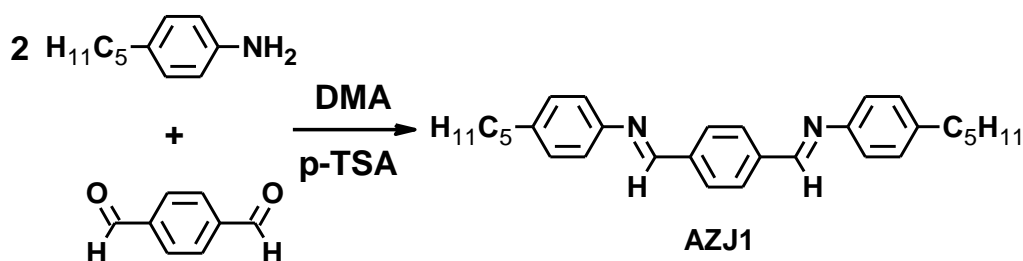


Figure 1. Scheme of AZJ1 synthesis.

Sample was characterized with ¹H NMR, using deuterated chloroform (CDCl₃) as a solvent with a Jeol ECZ-400 S spectrometer (¹H - 400 MHz) with delay time 5 s. Measurements were carried out at room temperature on 10-15% (w/v) sample solutions.

¹H NMR (400 MHz, CDCl₃), δ [ppm]: 8.52 (s, 2H, -HC=N-), 7.99 (s, 4H), 7.23-7.17 (m, 8H), 2.62 (t, 4H), 1.61 (m, 4H), 1.35- 1.30 (m, 8H), 0.89 (t, 6H).

¹³C NMR (75 MHz, CDCl₃, TMS) [ppm]: δ = 158.55 (HC=N), 149.24, 141.46, 138.61, 129.98, 128.96, 120.87, 35.46, 31.46, 31.18, 22.53, 14.03.

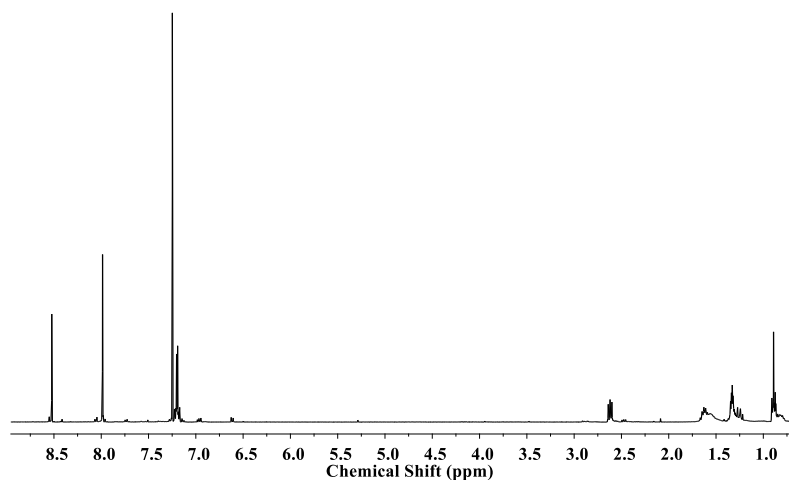


Figure 2. ^1H NMR of AZJ1 in CDCl_3 .

Spectroscopic characterization of AZJ1 at room temperature (FT-IR)

The investigated AZJ1 compound was preliminary studied by middle infrared absorption spectroscopy at room temperature in order to confirm its proper composition and molecular structure. The IR spectrum and tentative description of the observed bands are presented in Figure S3 and Table S1 in Supplemental Material. The spectrum consists mainly of bands connected to stretching and bending vibrations of aliphatic chains, aromatic rings and the $-\text{HC}=\text{N}-$ imine groups located between the aromatic rings. The most intensive bands at 852 and 838 cm^{-1} are connected to the $\omega(\text{CCH})_{\text{ar}}$ out of plane bending vibrations of 1,4-substituted benzene rings. Considering stretching vibrations within aromatic rings, several sharp bands of medium intensity between 1600–1490 cm^{-1} ascribed to $\nu(\text{C}=\text{C})_{\text{ar}}$ vibrations and several bands of low intensity between 3110–3000 cm^{-1} ascribed to $\nu(\text{CH})_{\text{ar}}$ vibrations are present. The characteristic strong band connected to the $\nu(\text{HC}=\text{N})$ stretching mode of the imine groups is located at 1624 cm^{-1} .

As the AZJ1 compound contains two terminal aliphatic chains, strong bands in the spectral range of 3000–2750 cm^{-1} connected to the $\nu(\text{CH}_2)$ and $\nu(\text{CH}_3)$ symmetric and asymmetric stretching vibrations can also be observed. In turn, the bands connected to $-\text{CH}_2$ and $-\text{CH}_3$ bending vibrations are visible in the range of 1470–1300 cm^{-1} in the IR spectrum. The characteristic rocking vibration $\rho(\text{CH}_2)$, which appears when long aliphatic chains are present, is split into two components what suggests existing of closely packed methylene chains. In addition to fundamental vibrations, overtones and combination tones are also present as low intensity bands located in three spectral ranges: 3280–3140 cm^{-1} , 2750–2500 cm^{-1} , and 2000–1640 cm^{-1} . Summing up, all functional groups expected in the IR spectrum of AZJ1 could be observed what confirms proper composition of the investigated compound.

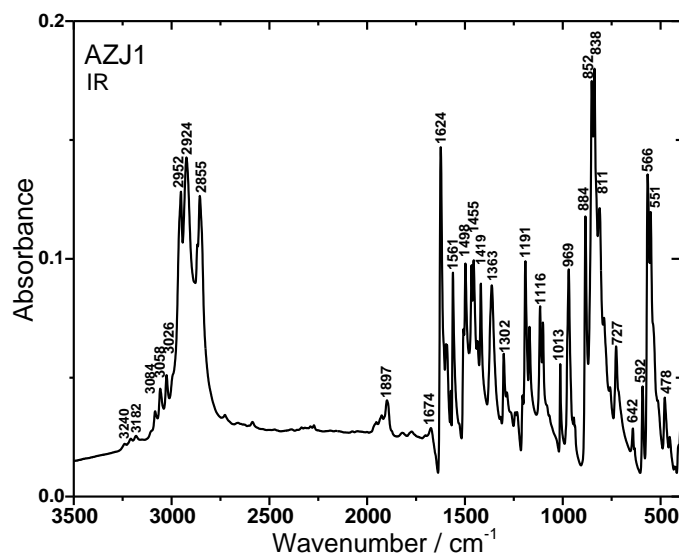


Figure 3. FT-IR spectrum of AZJ1 obtained at room temperature with marked positions of the most prominent bands.

Table 1. List of band positions (cm^{-1}) of the FT-IR spectrum of AZJ1 with tentative assignments based on literature [1–3].

Band position	Tentative assignments	Band position	Tentative assignments
3240 w	$2\nu(\text{HC}=\text{N})$	1244 w	-
3208 w	$2\nu(\text{C}=\text{C})_{\text{ar}}$	1233 w	-
3182 w	$2\nu(\text{C}=\text{C})_{\text{ar}}$	-	-
3106 w	$\nu(\text{CH})_{\text{ar}}$	1191 m	$\delta(\text{CH})_{\text{ar}}$ ip
3084 w	$\nu(\text{CH})_{\text{ar}}$	1170 m	$\delta(\text{CH})_{\text{ar}}$ ip
3058 w	$\nu(\text{CH})_{\text{ar}}$	1116 m	$\delta(\text{CH})_{\text{ar}}$ ip or $\nu(\text{CC})_{\text{aliph}}$
3026 w	$\nu(\text{CH})_{\text{ar}}$	1101 m	$\delta(\text{CH})_{\text{ar}}$ ip or $\nu(\text{CC})_{\text{aliph}}$
2993 sh	-	1013 m	-
2960 sh	$\nu_{\text{as}}(\text{CH}_3)$	977 sh	$\delta(\text{CH})_{\text{ar}}$ ip
2952 s	$\nu_{\text{as}}(\text{CH}_3)$	969 m	$\delta(\text{CH})_{\text{ar}}$ ip
2924 vs	$\nu_{\text{as}}(\text{CH}_2)$	884 s	$\omega(\text{CCH})_{\text{ar}}$
2868 sh	$\nu_{\text{s}}(\text{CH}_3)$	852 vs	$\omega(\text{CCH})_{\text{ar}}$
2855 s	$\nu_{\text{s}}(\text{CH}_2)$	838 vs	$\omega(\text{CCH})_{\text{ar}}$
2844 sh	$\nu_{\text{s}}(\text{CH}_2)$	811 s	$\omega(\text{CCH})_{\text{ar}}$
1953 vw	$2\tau(\text{CH}_3)$	789 m	-
1926 vw	$2\tau(\text{CH}_3)$	758 sh	-
1899 w	-	-	-
1674 w	$2\omega(\text{CCH})_{\text{ar}}$ $\nu(\text{HC}=\text{N})$	727 m	$\rho(\text{CH}_2)_{\text{long chain}}$
1624 vst		714 sh	$\rho(\text{CH}_2)_{\text{long chain}}$
1597 m	$\nu(\text{C}=\text{C})_{\text{ar}}$	642 w	-
1592 m	$\nu(\text{C}=\text{C})_{\text{ar}}$	633 sh	-
1572 w	$\nu(\text{C}=\text{C})_{\text{ar}}$	-	-
1561 m	$\nu(\text{C}=\text{C})_{\text{ar}}$	592 m	$\delta(\text{ring})_{\text{ar}}$ oop or $\delta(\text{CNC})$
1523 vw	$\nu(\text{C}=\text{C})_{\text{ar}}$	566 s	$\delta(\text{ring})_{\text{ar}}$ oop or $\delta(\text{CNC})$
1507 m	$\nu(\text{C}=\text{C})_{\text{ar}}$	551 s	$\delta(\text{ring})_{\text{ar}}$ oop or $\delta(\text{CNC})$
1498 m	$\nu(\text{C}=\text{C})_{\text{ar}}$	538 sh	-
1466 m	$\delta_{\text{as}}(\text{CH}_3)$	478 w	-
1455 m	$\sigma(\text{CH}_2)$	453 vw	-
1436 sh	-	389 w	-
1419 m	$\delta(\text{C}_{\text{ar}}\text{CH})$		
1371 m, sh	$\rho_{\text{s}}(\text{CH}_3)$		
1363 m	$\omega(\text{CH}_2)$		
1302 m	$\nu(\text{C}_{\text{ar}}-\text{N})$		
1285 w	$\nu(\text{C}_{\text{ar}}-\text{N})$		

(w – weak; sh – shoulder; m – medium; s – strong; vs – very strong; v – stretching; δ – bending; in plane (ip) modes: ρ – rocking, σ – scissoring; out of plane (oop) modes: ω – wagging, τ – twisting; ar – aromatic; aliph – aliphatic).

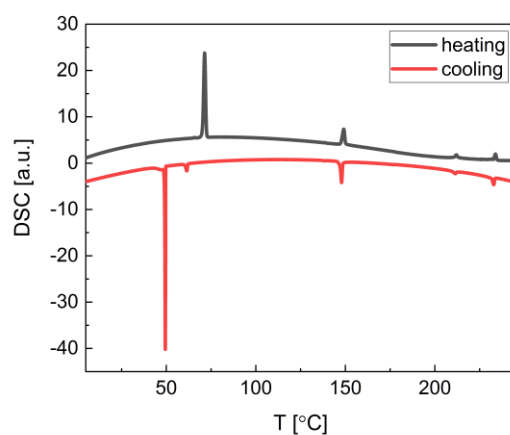


Figure 4. DSC curves of the imine AZJ1 registered during heating and cooling cycle at rate 10 °C/min.

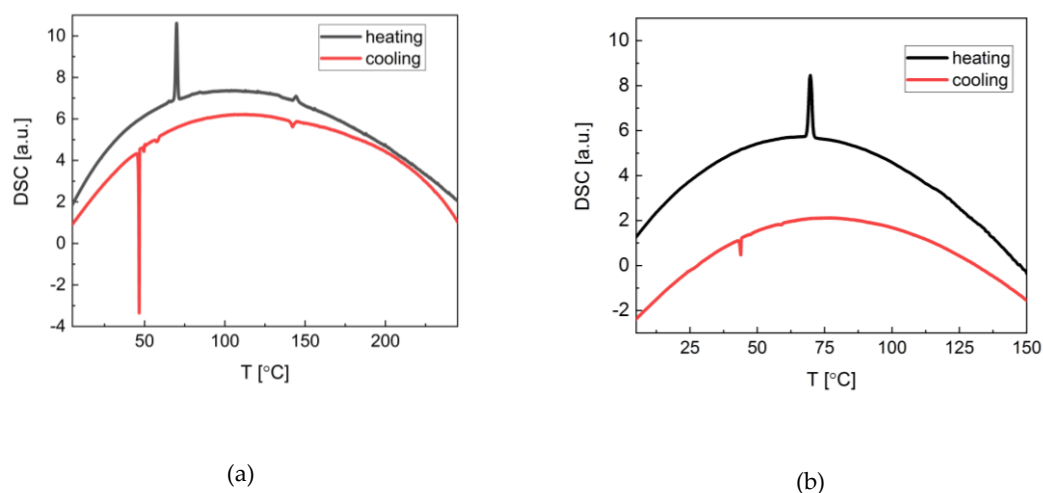
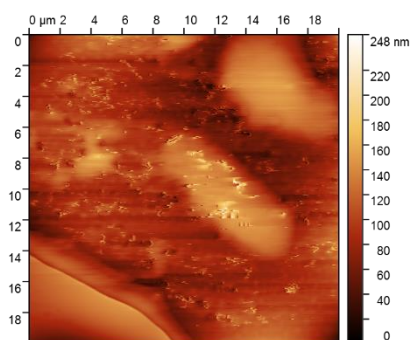


Figure 5. DSC curves of the imine AZJ1:TiO₂ (anatase) (a) and AZJ1:TiO₂ (rutile) (b) registered during heating and cooling cycle at rate 10 °C/min.



a) AZJ1 RMS 26.73 nm

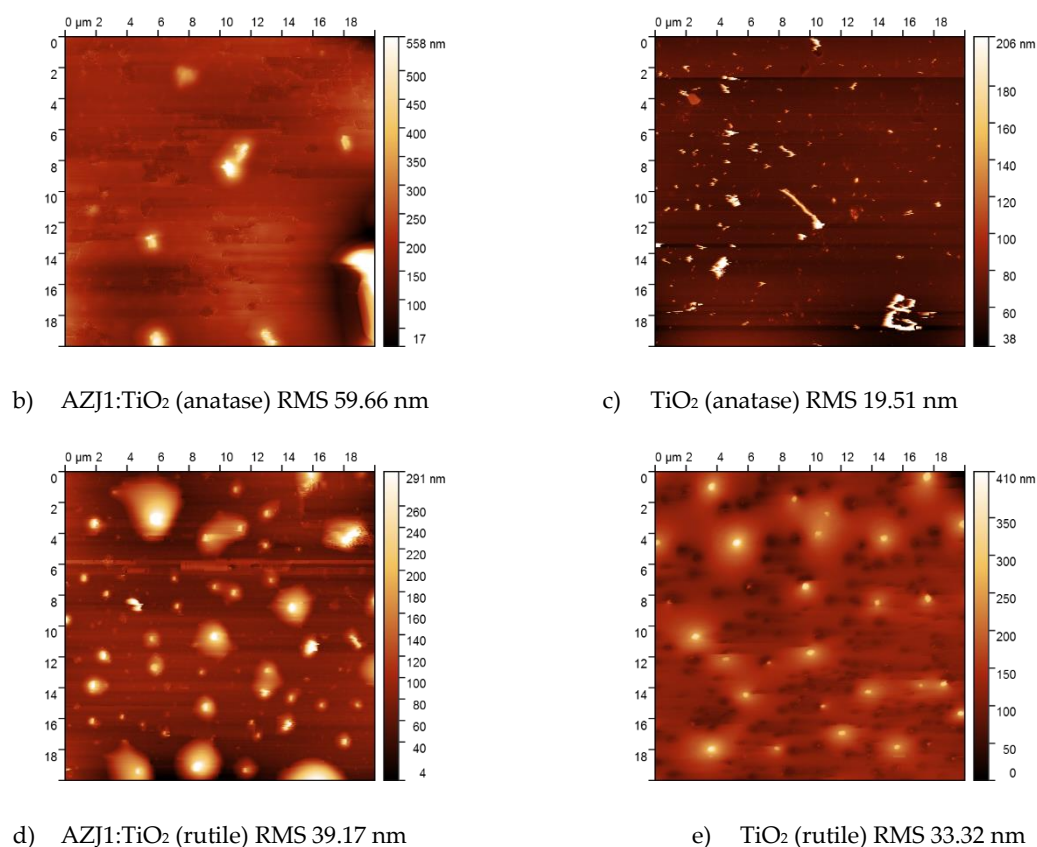


Figure 6. AFM topography images of the imine and its mixtures with TiO₂ with mass ratio 3:2: (a) AZJ1 molecule layer, (b) AZJ1:TiO₂ anatase mixture layer, (c) TiO₂ anatase layer, (d) AZJ1:TiO₂ rutile mixture layer, (e) TiO₂ rutile layer.

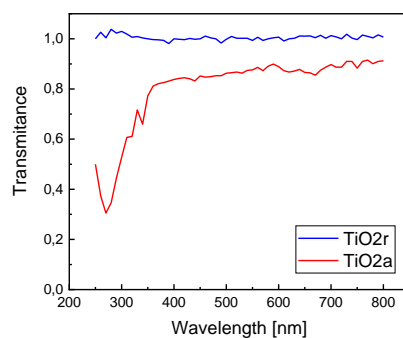


Figure S7. Transmission spectra of TiO₂ nanocrystals suspensions in chloroform, lower transmittance of anatase as compared to rutile for higher wavelengths results from higher scattering on larger particles.

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