5,6-Bis(5-methoxythiophen-2-yl)pyrazine-2,3-dicarbonitrile

(DPZ)

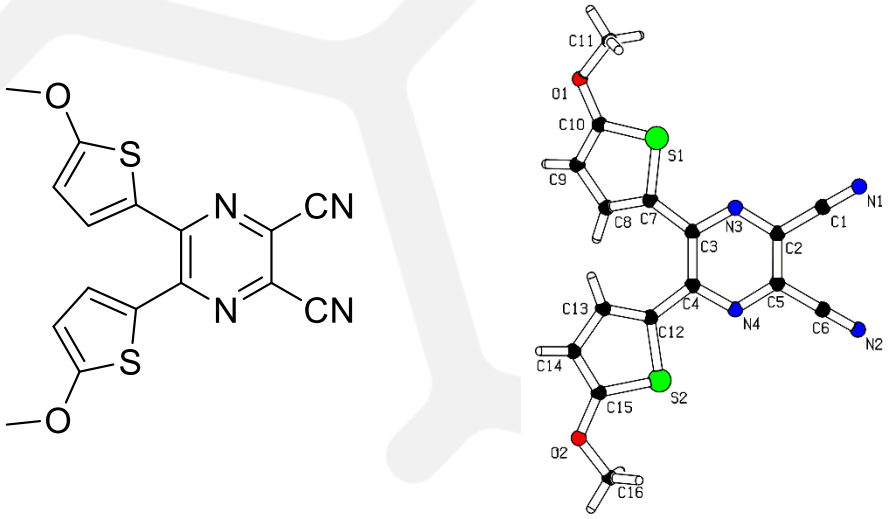

Figure 1. Chemical structure (left) and X-ray analysis (right) of DPZ catalyst.

Structural analysis:

TLC (SiO_2; CH_2Cl_2): R_f = 0.80;

^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.99 (s, 6H), 6.19 (d, *J* = 4 Hz, 2H), 7.68 ppm (d, *J* = 4 Hz, 2H);

^{13}C-NMR (125 MHz, $CDCl_3$): δ 60.8, 106.3, 113.7, 124.7, 126.3, 131.2, 146.7, 173.9 ppm;

IR (HATR): λ = 3071, 2227, 1467, 1403, 1380, 1211, 1067, 986, 784 cm^{-1};

HR-FT-MALDI-MS (DCTB) *m/z*: calculated for $C_{16}H_{10}N_4O_2S_2^+$ ([M]$^+$): 354.02404, found 354.02397;

Elemental analysis (%) calculated for $C_{16}H_{10}N_4O_2S_2$ (354.41): C 54.22, H 2.84, N 15.81, S 18.10; found C 54.33, H 2.90, N 15.82, S 18.05.

Storage:

In brown-glass vials at temperature ≈ 5 °C (no direct light irradiation).

Thermal, electrochemical, optical and calculated properties:

Table 1. Thermal and optical properties of DPZ catalyst.

.	T_m [°C][a)]	T_d [°C][b)]	λ_{max}^A [nm/eV][c)]	ε [mol^{-1}dm^{3}cm^{-1}][c)]	λ_{max}^F [nm/eV][c)]	Φ^F	Stokes shift [cm^{-1}/eV][c)]	$E_{0,0}$ [eV][d)]
DPZ	178	256	448/2.77	19000	552/2.25	0.02	4200/0.52	2.51/2.49

[a)] T_m = melting point. [b)] T_d = thermal decomposition. [c)] measured in CH_2Cl_2. [d)] Energy of excited singlet state; calculated as mean value between absorption and emission maxima; measured in CH_2Cl_2/CH_3CN.

Table 2. Electrochemical and DFT calculated data of DPZ catalyst.

	Electrochemical data							DFT calculated data[e)]			
	Ground state					Excited state		Ground state			
	$E_{1/2(ox1)}$ [V][a)]	$E_{1/2(red1)}$ [V][a)]	ΔE [V][b)]	E_{HOMO} [eV][c)]	E_{LUMO} [eV][c)]	E_{ox}^* [V][d)]	E_{red}^* [V][d)]	E_{HOMO}^{DFT} [eV]	E_{LUMO}^{DFT} [eV]	ΔE^{DFT} [V]	λ_{max}^{DFT} [nm/eV][f)]
DPZ	1.32	-1.07	2.39	-5.75	-3.36	-1.17	1.42	-5.90	-2.96	2.94	450/2.76

a) $E_{1/2(ox1)}$ and $E_{1/2(red1)}$ are half-wave potentials of the first oxidation and reduction; measured in CH_3CN, all potentials are given *vs*. SCE. [b)] $\Delta E = E_{1/2(ox1)} - E_{1/2(red1)}$ [c)] $-E_{HOMO/LUMO} = E_{1/2(ox1/red1)} + 4.429$ [d)] Redox potentials of excited state in CH_3CN approximated by using the energies of excited singlet state $E_{0,0}$; calculated: $E_{ox}^* = E_{ox} - E_{0,0}$ and $E_{red}^* = E_{red} + E_{0,0}$. [e)] Computed at DFT B3LYP/6-311++g(2df,p) level (scrf = solvent = CH_3CN). [f)] Calculated at TD-SCF (nstates = 8) B3LYP/6-31++g(2df,p) level in vacuum.

Table 3. DFT calculated data for radical cation of DPZ catalyst.[g)]

Comp.	$\Delta E^{\bullet+}$ [eV]	$E^{\bullet+}$(αHOMO) [eV]	$E^{\bullet+}$(αLUMO) [eV]	$E^{\bullet+}$(βHOMO) [eV]	$E^{\bullet+}$(βLUMO) [eV]
DPZ	5.57	-6.55	-3.61	-6.96	-5.27

Table 4. DFT calculated data for radical anion of DPZ catalyst. [g)]

Comp.	$\Delta E^{\bullet-}$ [eV]	$E^{\bullet-}$ (αHOMO) [eV]	$E^{\bullet-}$ (αLUMO) [eV]	$E^{\bullet-}$ (βHOMO) [eV]	$E^{\bullet-}$ (βLUMO) [eV]
DPZ	-3.20	-3.47	-1.91	-5.20	-2.05

Table 5. DFT calculated data for dianion and dication of DPZ catalyst. [g)]

Comp.	ΔE^{2-} [eV]	E^{2-} (HOMO) [eV]	E^{2-} (LUMO) [eV]	ΔE^{2+} [eV]	E^{2+}(HOMO) [eV]	E^{2+}(LUMO) [eV]
DPZ	-5.53	-2.61	-1.16	11.81	-7.91	-5.92

Table 6. DFT calculated data for triplet state of DPZ catalyst. [g)]

Comp.	ΔE^T [eV]	E^T(αHOMO) [eV]	E^T(αLUMO) [eV]	E^T(βHOMO) [eV]	E^T(βLUMO) [eV]
DPZ	1.66	-4.22	-2.68	-6.45	-4.52

[g)] Calculated using the DFT B3LYP/6-311++g(3df,2p) method.

Native data of performed analysis:

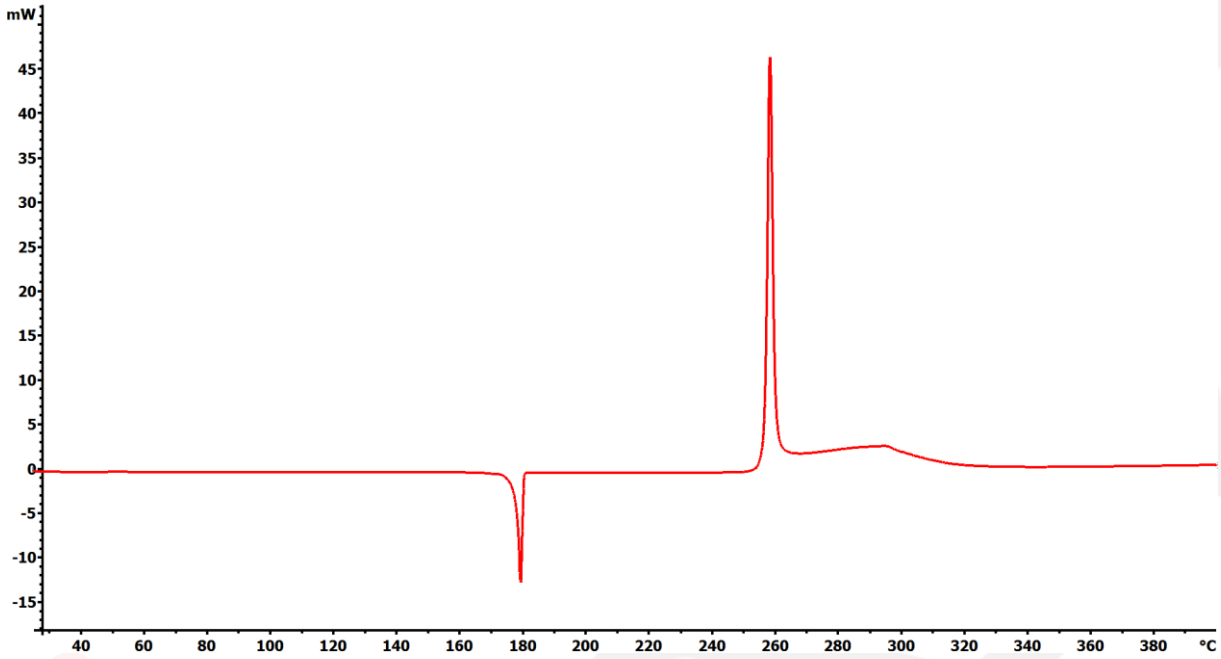

Figure 2. DSC thermograph of DPZ catalyst.

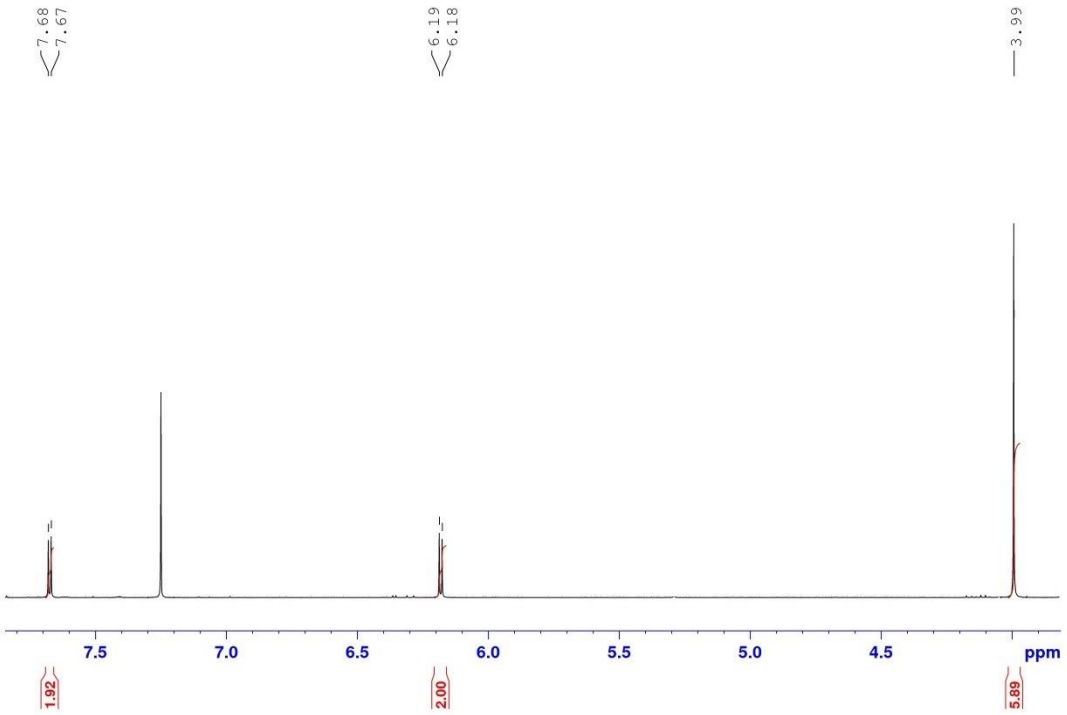

Figure 3. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) spectra of DPZ catalyst.

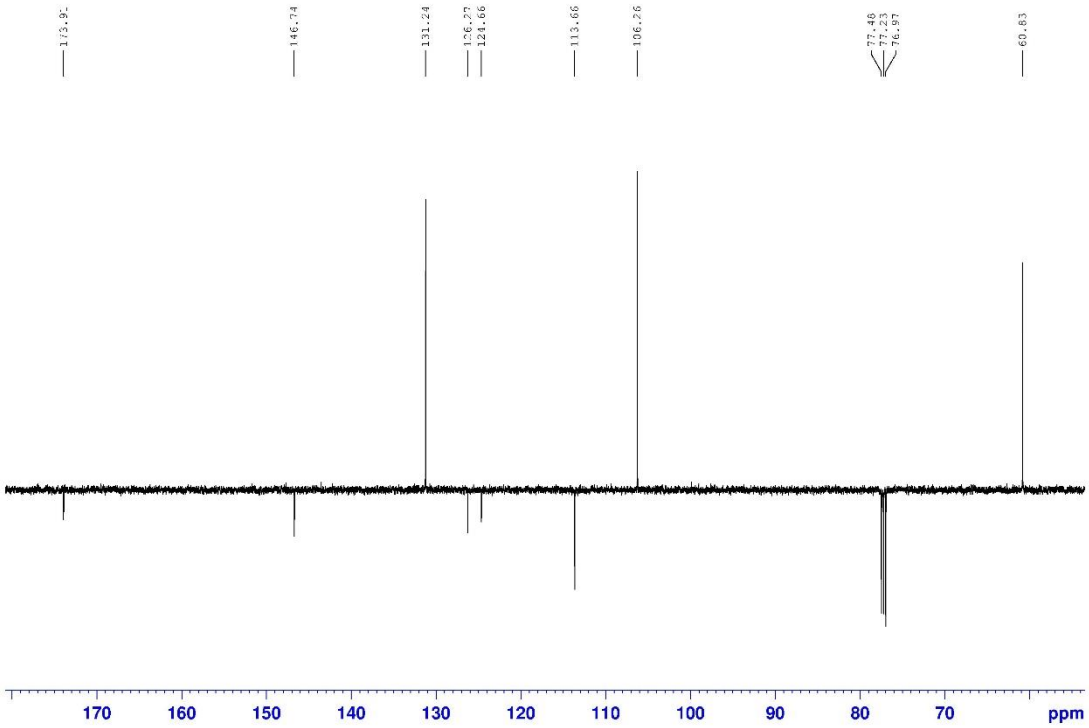

Figure 4. ^{13}C-NMR (APT, 125 MHz, $CDCl_3$, 25 °C) spectra of DPZ catalyst.

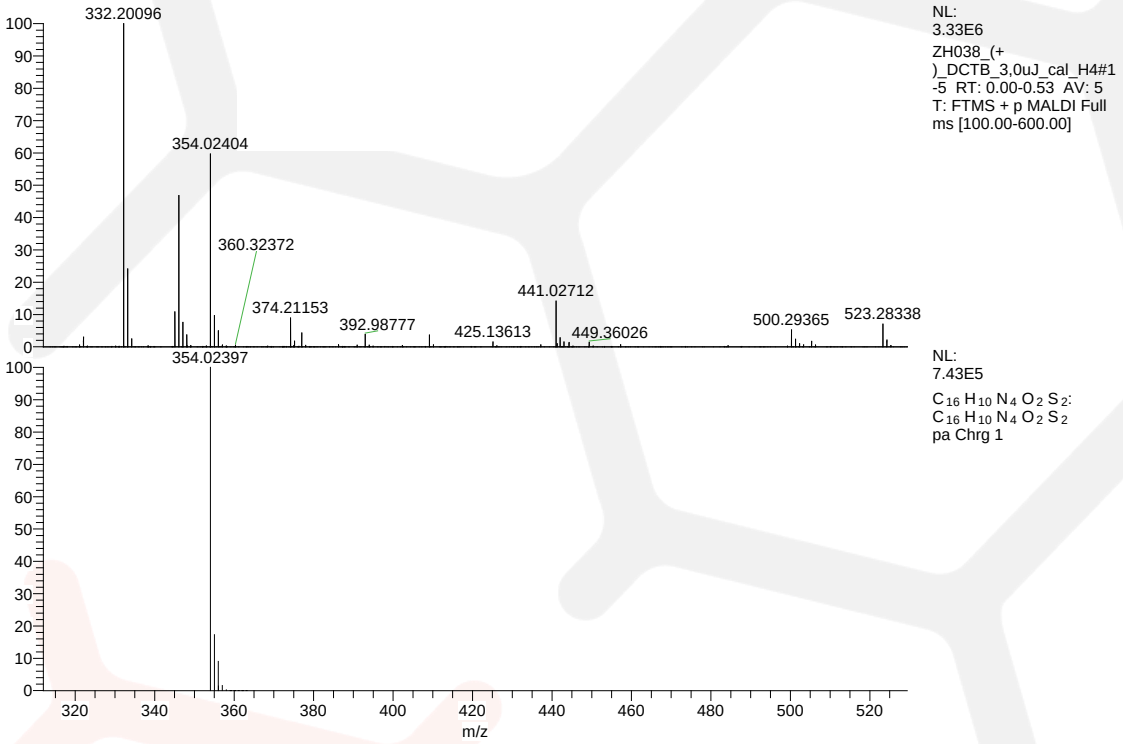

Figure 5. Experimental (up) and simulated (down) HR-FT-MALDI-MS spectra of DPZ catalyst.