

Supporting Information

Advances of the highly efficient and stable visible light active photocatalyst

Zr(IV)-Phthalate coordination polymer for the degradation of organic

Contaminants in water

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Section S1. XRD for the prepared Zr-Ph CP.

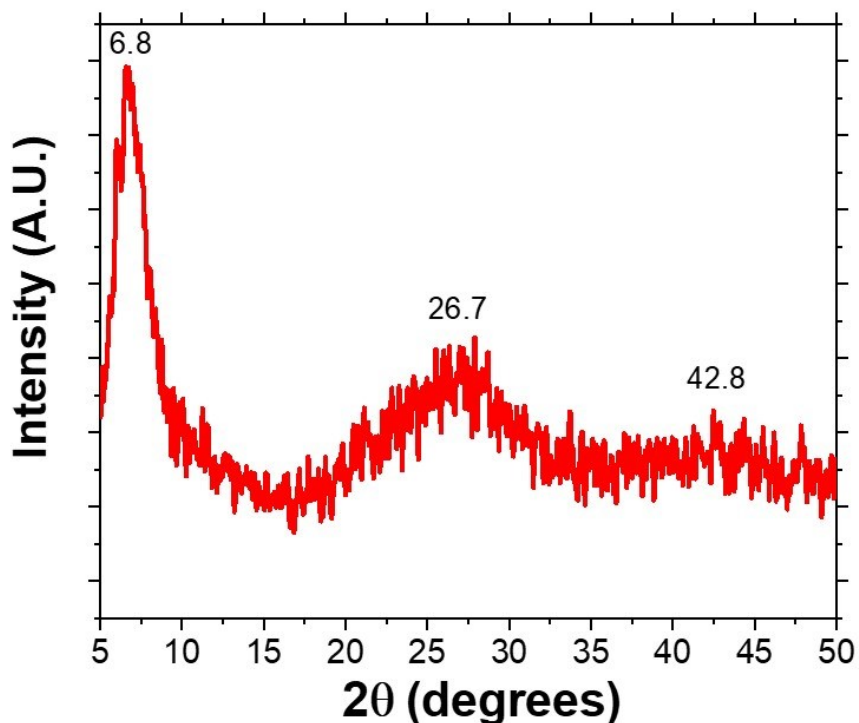


Figure S1. XRD pattern for the prepared Zr-Ph CP.

Section S2. Full Detailed Structural Analysis of Zr-Ph CP.

The successive preparation of Zr-Ph CP was confirmed and investigated via FTIR and Raman analysis. Table S1 represents the observed Raman and FTIR peaks and their possible assignments supported with references. A Raman spectrum can be divided into three main regions where the first one is the low wavenumber region (below 300 cm^{-1}), which is assigned to lattice vibrations. The disappearance and/or change of lattice vibration peaks upon formation of CP from phthalic acid indicate that crystal is changed by any means to form a new product[1-4]. As mentioned in literatures, the main lattice vibration bands for neat solid state phthalic acid are present at 137, 168, and 375 [5-8]. Upon formation of CP, on the other hand, two notable sharp peaks appear at 87, and 112 cm^{-1} . In addition to two weak peaks appear at 210, and 230 cm^{-1} within the lattice vibrations region of the product spectrum. Since lattice vibrations are unique for a given crystalline substance, this peak can be sought as identification of the formation of CP[1]. Moreover, the weak peaks at 210 and 230 cm^{-1} could be assignable to the $\text{Zr}^{+4}\cdots\text{O}$ vibration appears, which may indicate that not only the π and π^* orbitals but also the oxygen lone pair electrons of carboxylate groups take part in the interaction with the Zr^{+4} [9-11]. In general, the observed dramatic change in the lattice vibrations region of the product, MOF, with respect to that of phthalic acid indicates a successful synthesis of crystalline Zr-Ph CP. In addition, it may confirm the complete conversion of phthalic acid to a new pure product since no lattice vibration peaks of phthalic acid are still present in Zr-Ph CP spectrum.

The second region of Raman spectrum may be assigned as the fingerprint region which lies in the range $300\text{-}1800\text{ cm}^{-1}$ [12, 13]. Typical Raman peaks of neat solid state phthalic acid normally appear at 372, 438, 547, 643, 694, 739, 772, 799, 894, 1005, 1045, 1142, 1175, 1264, 1304, 1427, 1496, 1591, and 1710 cm^{-1} [6, 14-16].

On the other hand, the Raman peaks of Zr-Ph CP appears at 378, 412, 436, 646.5, 769, 798, 858, 1008, 1167, 1263, 1302, 1411.5, 1432.5, 1449, 1495, 1585, 1599, 1639.5, and 1662 cm^{-1} . Regarding the Raman spectrum of Zr-Ph CP, it is obvious that the phthalic acid fingerprint peaks are collectively still present with some shifts. Furthermore, these peaks become more intense relative to those of phthalic acid. The observed weak peaks at 378, 142, and 436 could be attributed to C-H out of plane bending [9, 14]. Furthermore, the COO^- Bending modes were

observed in Raman spectrum at 646.5, 769, 798, and weak shoulder at 858 cm^{-1} . These peaks are confirmed as the corresponding within the FTIR spectrum, were detected at 551.4, 636.4, 664.8, 734.2, 793, and 833.4 cm^{-1} . Furthermore, these results also provide clear evidence of the efflorescence of phthalic acid as phthalate anions coordinated with metallic cations incorporated within the MOF structure [9, 11, 14, 17]. Moreover, the C-H bending modes and ring breathing modes were not notable in Raman spectrum, but observed in the FTIR spectrum at 895.8, 973.8, 1003.5, and 1046 cm^{-1} [3, 9, 11].

Additionally, the ortho-disubstituted benzene vibration observed at 1146.7 and 1271.4 cm^{-1} in the FTIR spectrum and confirmed in the Raman spectrum as observed at 1167, 1263 cm^{-1} [3, 9, 10, 14, 17]. Further COO^- stretching modes and benzene ring stretching modes were observed in the Raman spectrum at 1411.5, 1432.5, 1449, 1585, 1599, 1639.5, 1662 cm^{-1} . In addition, the FTIR confirm theses assignments at 1400.4, 1493.9, 1543.5, 1578, and 1672 cm^{-1} [3, 9-11, 18]. The absence of the characteristic carbonyl stretching frequency at $\sim 1710\text{cm}^{-1}$ confirm to the presence of phthalate anion $^{2-}$ in CP structure incorporated with metallic cations [3, 19]. The presence of more than two bands in the carboxylate stretching region suggests the existence of at least two different carboxylates or two different complexes [10]. In addition, when carboxyl groups interacted with metallic ion species, it may hinder the carbonyl stretching [10]. The possibility of having phthalate anions coordinated with metallic cations incorporated within the MOF structure was confirmed again as some references referred the assignment of some of the pervious peaks to stretching modes of COO^- - metal coordination [3, 9-11].

The possible COO^- - Zr^{4+} coordination bonding scheme could be proposed as being a σ -coordination, via the donation of oxygen lone pair electrons to Zr^{4+} , and the other a π -coordination via the donation of π -electrons of the carboxylate group(s) to Zr^{4+} accompanied by a

metal-to- carboxylate π^* back-donation [11]. Based on the binding mechanism a different orientation of the adsorbing species on the surface could be adopted: a σ type coordination will result in a vertical orientation on the surface, while a π type coordination will result in a parallel orientation. The last region over 1800cm^{-1} comprises mainly the C–H vibrations. Nonetheless, it is informative that the ring C–H stretching bands such are observed distinctly at 3082 and 3034cm^{-1} in case of Raman spectrum of neat solid state phthalic acid and at 3068cm^{-1} in the FTIR spectrum[2, 6, 9].

At the same region, it was obvious that the O-H stretching band at $\sim 3500\text{cm}^{-1}$ is also obscured in the Zr-Ph CP spectrum [9], which may be attributed due to the distortion of O–H groups of phthalic molecule in the Zr-Ph CP structure. Hence, there are probably no conditions for the strong coupling giving O-H bands caused by intermolecular hydrogen bonds O–H...O type, like in the crystal of phthalic acid alone [20]. Moreover, The weak IR absorption bands appear near 2525cm^{-1} and 2888cm^{-1} are corresponding to O-H stretching of carboxyl group and C-H stretching (superimposed upon O-H stretching), respectively [21]. These weak peaks may indicate possible traces residual unprotonated hydroxyl group incorporated in CP structure. All these data confirm that the bridging coordination is realized via the hydroxy oxygen atoms of phthalic acid, which being deprotonated and the COO^- group is acting as a unidentate ligand [22]. The significant change in this region of the Raman and FTIR spectra of the Zr-Ph CP confirms the difference of orientation of phthalate molecules in the product rather than of pure phthalic acid. Moreover, when a ligand coordinates to a metal atom, new modes of vibration not present in the free ligand may become infrared or Raman active [23]. The previous discussion leads to the conclusion and confirmation of coordination of Zr^{4+} cations with COO^- groups as

expected merely because of the coordination of COO⁻ of phthalate molecules with Zr cations, which changes the electronic environment of the phthalate.

Table S1 Assignment of the Raman and FTIR peaks.

FTIR ν, cm ⁻¹	Raman ν, cm ⁻¹	Assignment	References
	85	lattice vibrations	Zr-Ph CP
	114	lattice vibrations	Zr-Ph CP
	163(vw)	lattice vibrations	Zr-Ph CP
	210(vw)	Metal –O coordination	[9, 11]
	231(vw)	Metal –O coordination	[9-11]
	378(w)	C-H out of plane Bending	[9, 14]
	412(vw)	C-H out of plane Bending	[9]
	436 (vw)	C-H out of plane Bending	[9, 14]
551.4s		COO ⁻ Bending mode	[9]
636.4w	646.5	COO ⁻ Bending mode (COO ⁻ Metal coordination)	[9, 17]
664.8w		COO ⁻ Bending mode	[9]
734.2s	769	COO ⁻ Bending mode (COO ⁻ Metal coordination)	[11, 17]
793	798	COO ⁻ Bending mode (COO ⁻ Metal coordination)	[11, 17]
833.4vw		COO ⁻ Bending mode	[14]
	858(w-sh)	Ring breathing	[9]
		Bending mode COO ⁻	[9, 11, 14]
895.8s		C-H Bending	[9]
973.8w		C-H Bending	[9]
1003.5w	1008(vw)	C-H Bending	[3, 9, 11]
1064s		Ring breathing	[9-11]
1146.7s	1167	ortho-disubstituted benzene vibration	[24]
1271.4vs	1263	ortho-disubstituted Benzene vibration	[3, 9, 10, 14, 17]
	1302(w)	O-H Bending deformation	[14]
1400.4vs		ν COO ⁻	[3, 9, 10]
		stretching COO ⁻ Metal coordination	[10]
	1411.5(w)	ν COO ⁻	[10]
	1432.5(w)	ν COO ⁻	[10]
	1449(w)	Benzene ring stretching	[10]
1493.9w	1495	Benzene ring stretching	[3, 9, 10, 18]
		ν COO ⁻ Asymmetric (metal-carboxylate coordination)	[11]
1543.5w		stretching COO ⁻ Metal coordination	[3, 9-11]
1578.9s	1585(sh)	Benzene ring stretching	[3, 9]
		stretching COO ⁻ Metal coordination	[10]
	1599	ν COO ⁻	[10, 18]
	1639.5(vw)	ν C=O	[6, 14]
1672.5s	1662(vw)	ν C=O	[6, 10, 15]
2522vw		O-H stretching of carboxyl group	[21]

Section S3. BET and pore size distribution analysis.

Figure S2 A shows the BET adsorption-desorption isotherm of Zr-Ph CP. The BET surface area was 8 m²/g. Figure S2 B shows the pore size distribution of Zr-Ph CP, it was estimated to be 3 nm with is larger than MB and MO.

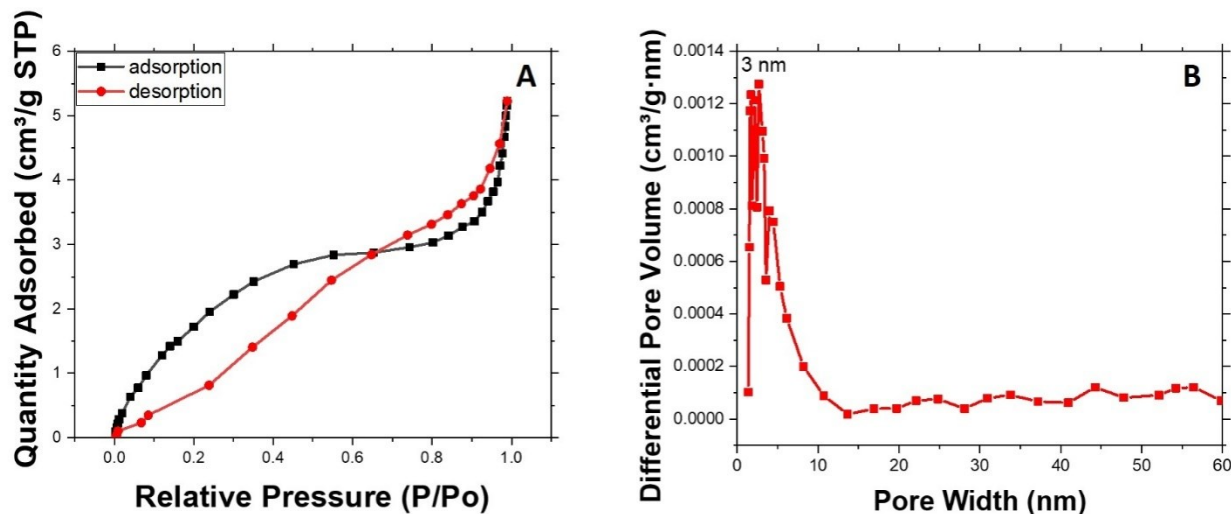


Figure S2. (A) N₂ isotherms, and (B) pore size distribution of the Zr-Ph CP.

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