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A new nanohybrid material constructed from Keggin-type polyoxometalate and Cd(II) semicarbazone Schiff base complex with excellent absorption properties for the removal of cationic dye pollutants

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- 11

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12 ABSTRACT

13 A novel nanohybrid material containing a Cd(II) semicarbazone Schiff base complex and 14 phosphomolybdic acid, $[Cd(H_2L^+)_6][H_2L^+]_4[PMo_{12}O_{40}]_4.18CH_3OH 4H_2O$ (1), [HL= pyridine-2-15 carbaldehyde semicarbazone] was prepared by a simple sonochemical route and characterized by 16 ¹HNMR, ¹³CNMR, FT-IR, UV-vis, PXRD, FESEM, TG-DTA and BET-BJH surface area analysis. 17 Also the single crystal 1, was characterized by single-crystal X-ray diffraction analysis. It crystallizes 18 in the triclinic system with space group P-1 and is assembled into 3D supramolecular structure via 19 hydrogen intermolecular interactions. The nanohybrid 1 was tested for the adsorption and removal of 20 organic dyes such as methylene blue (MB), Rhodamine B (RhB) and methyl orange (MO) from 21 aqueous solutions. The effects of parameters such as the dosage of adsorbent, the initial concentration 22 and pH of dye solution were investigated on the removal efficiency of methylene blue. The 23 nanohybrid 1 exhibited excellent adsorption ability towards cationic dyes. Moreover, it could be 24 easily separated from the reaction solution and recycled up to three times without significant loss of 25 adsorption activity.

Keywords: Nanohybrid material, Polyoxometalate, Single crystal, Adsorption activity, Cationic dye
pollutants.

28

29 1. Introduction

Water pollution with organic compounds has been one of the challenging environmental issues in many countries [1-3]. In particular, synthetic dyes have become major water pollutants generated mainly from textile dyeing, paper printing, color photography and petroleum industries because about 10-15% of the total world production of synthetic dyes is

34 lost during textile dyeing, more precisely, released into the textile effluents [4,5]. A wide 35 variety of synthetic dyes, namely, azo, polymeric, anthraquinone, triphenylmethane and 36 heterocyclic dyes, are used in textile dyeing processes [6,7]. Therefore, continuous discharge 37 of dye-bearing effluents from textile industries into natural stream and rivers poses severe 38 environmental problems because synthetic dyes are considered to be one of the poisonous 39 and harmful compounds for water, soil and human life [8]. Moreover, synthetic dyes can also 40 hinder sunlight's penetration into the water, leading to the eutrophication and the die-off of plants and animals [9,10]. Due to the complex nature and difficulty of removal of synthetic 41 42 dyes by conventional methods, textile dyeing industry is presently facing problems to safe 43 discharge of wastewater. So far, there are many techniques which have been reported on the 44 effective elimination of hazardous substances from aqueous solutions such as biological or 45 physical methods, photocatalytic degradation, sonocatalytic degradation, oxidation, 46 adsorption and so on [11-20]. Among the proposed techniques, adsorption is the procedure of 47 choice because it can reach good results and high efficiency using, inexpensive, eco-friendly 48 and simple materials [21–23]. The goal is to find a desirable adsorption material, which not 49 only is able to reduce the pollutant organic dyes with high efficiency and low loss, but also 50 allows for selective separation and recovery of raw materials [24].

51 In recent years, polyoxometalate (POM)-based inorganic-organic hybrid nanomaterials 52 have attracted considerable scientific attention in the field of environmental remediation and 53 removing organic dyes pollutants [25-28]. POMs as an outstanding family of metal oxide 54 clusters with controllable shape and size, highly electronegative, rich redox, photoactive, 55 oxo-enriched surfaces, and abundant topologies, have been employed in many research fields, 56 such as nonlinear optics, magnetism, catalysis, biological medicine and materials science [29-57 32]. Up to now, a variety of strategies have been developed and used to assemble POM-based 58 hybrid materials by controlling reaction factors, such as metal ions, organic ligands, POM

59 species, pH value and temperature, molar ratio of raw materials and reaction environment 60 [33-36]. Keggin-type POMs can coordinate to transition metals using their terminal or 61 bridging oxygens [37,38]. A prominent subclass of Keggin-type POMs is polyoxomolybdates 62 with range of intriguing topologies and structures based on coordination bonds or hydrogen 63 bonds probably due to their spherical surfaces. So far, there are many techniques which have 64 been reported for synthesis of inorganic-organic hybrid materials. Many POM-based hybrids 65 have been constructed under the commonly used solvothermal methods or some structures 66 have been synthesized via slow-diffusion processes, which both methods take days or weeks 67 to complete a hybrid material synthesis reaction, making the industrial preparation of these 68 materials difficult [39-41]. Recently, sonochemical synthesis as an alternative means to the 69 general synthetic methods has been used in the preparation of many materials. Ultrasound 70 induces chemical changes due to cavitation phenomena involving the formation, growth, and 71 instantaneously implosive collapse of bubbles in liquid, which can generate local hot spots 72 having a temperature of roughly 5000 °C, pressures of about 500 atmosphere, and a lifetime 73 of a few microseconds. This method for preparation of coordination compounds may be had 74 some advantages such as: it takes place in shorter reaction times, produces better yields and 75 also it may produce the coordination compound at nano-size scale [42-44]. Introduction of 76 Schiff base ligands into the chemistry of POMs opens a new direction for the synthesis of 77 hybrid materials with desirable abilities in different applications, which only a few results are 78 reported up to now [45-47].

Herein the progress in synthesis of hybrid material based on Schiff base organic ligands and polyoxomolybdates as inorganic building blocks is referred. We report a new nanohybrid material, $[Cd(H_2L^+)_6][H_2L^+]_4[PMo_{12}O_{40}]_4.18CH_3OH.4H_2O$ (1), containing Cd(II) pyridine-2carbaldehyde semicarbazone Schiff base complex and Keggin-type phosphomolybdic acid. The nanohybrid 1 was synthesized via a sonochemical synthesis route with a good yield

within a short time. Furthermore, the suitable single crystal **1**, were synthesized via the branched tube method for X-ray crystallography analysis. The compound **1** was fully characterized and its adsorption ability towards some of organic dye pollutants in aqueous solution was investigated.

88

89 **2. Experimental**

90 **2.1. General**

91 All chemicals and solvents were of reagent grade and used as received from Merck or Fluka. ¹HNMR and ¹³CNMR spectra were recorded on a Bruker Avance 400-MHz and 92 Bruker AVANCE 300-MHz instrument, at room temperature with the signal of free 93 94 deuterated dimethyl sulfoxide, $(CD_3)_2SO$ solvent by using TMS as internal reference. 95 Fourier-transform infrared spectra were recorded on Shimadzu FT-IR 8400S (Japan) with temperature controlled high sensitivity detector (DLATGS detector) and resolution of 4 cm⁻¹ 96 in the scan range of 500-4000 cm⁻¹ using KBr pellet. The nanohybrid and single crystal 1, 97 98 were characterized using X-Ray diffract meter Philips X-Pert (Philips 8440) with radiation 99 Cr-Ka radiation, $\lambda = 2.289$ Å in the range of $2\theta = 5^{\circ}-70^{\circ}$ at room temperature. The SEM 100 micrographs were obtained with Field emission scanning electron microscope (MIRA3 101 TESCAN) equipped with a link energy-dispersive X-ray (EDX) analyzer. The Brunauer-102 Emmett-Teller surface area (BET) of the powders was analyzed by nitrogen adsorption on a 103 Micromeritics ASAP 2020, USA. Thermal analysis (TG–DTA) was carried on a Bahr STA-104 503 instrument in air atmosphere with heating rate of 10 °C/min in the range of 40-820°C. 105 Vibrating sample magnetometer (VSM, Iran Meghnatis Daghigh Kavir Company) was 106 employed to measure the magnetic parameter at room temperature. A multiwave 107 ultrasonic generator (Bandeline GM 2200) equipped with a converter/transducer and titanium 108 oscillator operating at 20 kHz with a maximum power output of 200 W was used for the

109	ultrasonic	irradiation.	UV-vis	spectra	were	recorded	on	a	Carry	100	Varian
110	spectropho	tometer in a v	vavelengtl	n range of	200-80	00 nm at ro	om te	mp	erature.		

111

112 **2.2. Synthesis of ligand HL**

113 Schiff base HL [HL: pyridine-2-carbaldehyde semicarbazone ligand] (Scheme S1), was 114 prepared vis the condensation of pyridine-2-carbaldehyde with semicarbazide hydrochroride 115 under refluxing conditions according to the reported procedure [48-51]. Yield: 80%. Anal. Calc. for C₇H₈N₄O: C, 45.7; H, 4.5; N, 30.1%. Found: C, 45.9; H, 4.3; N, 30.3%. 116 Characteristic FT-IR data (KBr, cm^{-1}): 3321 m, v(NH₂); 3160 m, v(NH); 1612 s, v(C=N); 117 1701 s, v (C=O); 1168 m, v(N–N); v(N _{pyridine ring}) 622 w. ¹³CNMR: δ (ppm) 146.5 C(1); 118 119 126.1 C(2); 129.5 C(3); 125.8 C(4); 147.0 C(5); 142.6 C(6); 156.4, C(7). ¹HNMR: δ (ppm) = 8.75 (d, 1H, C(1)H); 7.85 (t, 1H, C(2)H); 8.55 (t, 1H, C(3) H); 8.29 (d, 1H, C(4)H); 8.03 (s, 120 121 1H, C(6)H); 11.28 (s, 1H, NH).

122

123 **2.3. Synthesis of nanohybrid** (1)

To preparation of nanohybrid 1, 10 mL methanolic solution of cadmium(II) acetate 124 125 dihydrate (0.02 M) was sonictaed in a high-density ultrasonic probe, operating at 20 kHz with 126 a maximum power output of 200 W [52,53]. To this solution, 10 mL methanolic solution of 127 HL (0.01 M) and 20 mL methanolic solution of phosphomolybdic acid (0.1 M) were added 128 dropwise, respectively and the mixture was sonicated for 30 min. Then, the dark yellow 129 precipitate was collected, filtered and washed with methanol and dried in air. Yield 65%. FT-IR data (KBr, cm⁻¹): 3460 m, v (NH₂); 3106 m, v(NH); 1623 s, v (C=N); 1686 s, v (C=O); 130 1164 m, v(NN), 1080 s, v (P-O_a); 981 s, v (Mo-O_t); 894 s, v (Mo-O_a) and 810 cm⁻¹ s, v 131 132 $(Mo-O_b).$

134 **2.4. Synthesis of single crystal (1)**

135 For the synthesis of compound 1 as suitable single crystal for structure analysis, the H 136 shaped branched tube is used [48, 49, 54-56]. HL ligand (0.04 g, 0.2 mmol) was placed in 137 one arm of a branched tube and mixtures of cadmium (II) acetate dihydrate (0.18 g, 0.6 138 mmol) and phosphomolybdic acid (0.36 g, 0.2 mmol) in the other arm of tube. Then, about 139 30 mL of methanol was carefully added, so that the bridge of the tube was filled. Then, the 140 tube was sealed and the arms were immersed in a bath at 60 °C, while the bridge was at 141 ambient temperature. After three days, polygon shape dark yellow crystals were deposited in 142 the cooler bridge, which were filtered off, washed with methanol and air dried. Yield: 40%. Characteristic FT-IR data (KBr, cm⁻¹): 3457 m, v(NH₂); 3106 m, v(NH); 1623 s, v(C=N); 143 144 1686 s, v(C=O); 1164 m, v(NN), 1080 s, v(P-O_a); 981 s, v(Mo-O_t); 894 s, v(Mo-O_a) and 812 cm⁻¹ s, v(Mo–O_b). ¹³CNMR: δ (ppm) 145.5 C (1); 125.8 C (2); 130.5 C (3); 124.9 C (4); 145 148.0 C (5); 143.4 C (6); 156.4, C (7). ¹H NMR: δ (ppm) = 8.77 (d, 1H, C(1)H); 7.84 (t, 1H, 146 147 C(2)H); 8.45 (t, 1H, C(3) H); 8.33 (d, 1H, C(4)H); 7.94 (s, 1H, C(6)H); 11.23 (s, 1H, NH); 7.00 (s, N pyridine ring NH), and for the methanol and water molecules 3.15 (s, H (C)H); 4.10 (s, 148 149 H (O)H).

150

151 **2.5. X-ray structure analysis**

The selected single crystal 0.49 x 0.32 x 0.20 mm³ was mounted on a fiber glass and placed on a four-cycle diffractometer Gemini (Rigaku Oxford Diffraction). Due to high absorption we used Mo K_{α} radiation ($\lambda = 0.71073$) from a sealed X-ray tube, monochromated with a graphite monochromator, collimated with a Mo-Enhance collimator, and detected with a CCD detector Atlas S1. Superflip [57] was used for structure solution by charge flipping, Jana2006 [58] for structure refinement and interpretation, Diamond4 (Diamond - Crystal and Molecular Structure Visualization. Crystal Impact - Dr. H. Putz & Dr. K. Brandenburg GbR,

Kreuzherrenstr. 102, 53227 Bonn, Germany, http://www.crystalimpact.com/diamond) for plotting. Structure analysis was quite standard, the $PMo_{12}O_{40}$ did not exhibit disorder sometimes found for this kind of compounds, and the organic part could be determined without problems due to good quality of data. Oxygen atoms of some CH₃OH molecules were disordered. We found also some isolated atoms, probably lattice water, whose hydrogen atoms could not be determined. Hydrogen atoms attached to carbon were kept in geometrically expected positions with $U_{iso} = 1.2|*U_{eq}$ of their parent atoms.

166 Hydrogen atoms attached to nitrogen atoms were mostly invisible in difference Fourier 167 maps due to the presence of heavy atoms in the structure. However, NH groups of N₂, N₃, N₄, 168 N_{10} and N_{11} as well as NH_2 groups of N_{14} , N_{13} , N_{18} , N_{19} and N_9 have been confirmed by spectroscopy. While atoms of NH could be attached geometrically, it was impossible for NH₂ 169 170 because this group is usually deviated of the triangular symmetry. Refinement of NH₂ groups 171 with distance restraint but refined positions lead to unreasonable geometry. Because for both 172 groups hydrogen atoms were equally invisible in the difference Fourier map, we decided to 173 omit all hydrogen atoms attached to nitrogen. With the neutral ligand HL, the charge of the 174 compound would be negative. In order to reach the charge balance, we tested possibility that 175 the nitrogen atoms of the aromatic rings, could be protonated. A summary of the key 176 crystallographic information, selected bond lengths and bond angles and also selected hydrogen bonding parameters of 1, are listed in Tables 1 - 3. 177

178 **2.6. Adsorption tests**

Freshly prepared compound **1** (30 mg) were transferred into 50 mL of aqueous solution of different dyes as methylene blue (MB), rhodamine B (RhB) and methyl organge (MO) with initial concentration of 25 mg L^{-1} . The mixture was stirred gently with the speed of 300 rpm at 25 °C. To prevent photodegradation of dyes by nanohybrid **1**, the dye solution was kept from light by being wrapped with dark paper during the adsorption tests. After soaking for

short time ranging from 30 seconds to 10 minutes, and in several intervals, the samples were separated through centrifuge to remove the suspended particles. Then the upper clear solutions were analyzed by a UV-vis spectrophotometer. The dye concentration was determined by using Carry 100 Varian spectrophotometer. The concentrations of MB and MO in the solution, were determined as a function of adsorption time from the change in absorbance at 664 and 553 nm for MB and RhB solution respectively at pH= 6 and absorbance at 463 nm for MO solution with pH= 5.

Other experiments with different dosage of compound **1**, such as 15, 30 and 45 mg towards adsorption of MB, were carry out. Furthermore, different concentration of MB dye solutions 25, 35 and 45 mg L^{-1} were prepared for investigate the ability of synthesized nanohybrid **1**, towards removal of MB molecules. Also for study the effects of initial solution pH on the adsorption process, several experiments were carry out. The initial pH of MB solution was adjusted to values in the range of 2–10 by dropwise adding 0.1 mol/L of NaOH or 0.1 mol/L of HCl solutions.

198 The amount of dye adsorbed per unit mass of nanohybrid material (q) and the dye 199 removal efficiency (R) could be calculated by applying the Eqs. (1) and (2), respectively:

200
$$q_t (mg/g) = V(C_0 - C_t)/m$$
 (1)

Where C_0 and C_t (mg/L) are the dye concentrations at initial and t time, respectively, m (g) represents the mass of the adsorbent and V (L) is the volume of dye solution.

After each adsorption experiments, the hybrid material **1**, loaded with MB was separated from the dye solutions by centrifugation and washed several times with water and ethanol at room temperature. Then the regenerated compound **1**, was dried overnight at 70 °C and reused for the next adsorption experiments. The structural details and nature of some organic pollutants used here, are listed in Table S1.

209

210 **3. Results and discussion**

211 **3.1. Synthesis** 212

The nanohybrid material **1**, was prepared by the sonochemical route and also suitable single crystal **1**, was synthesized for structure determination. The FT-IR and PXRD results confirmed the same composition for both synthesized samples.

216 **3.2.** Crystal structure description of compound 1

The structure of 1, determined by X-ray single crystal structure analysis and the crystal 217 218 data and structure refinement of 1, are summarized in Table 1. The compound crystallizes in 219 the triclinic space group P-1. As shown in Fig. 1 (a), the symmetric unit of 1, is consists of one Cd (II) center coordinated to six protonated ligands H_2L^+ , two isolated H_2L^+ , two 220 saturated Keggin-type polyoxoanions $PMo_{12}O_{40}^{3-}$, nine isolated methanol molecules which 221 222 two of them disordered, and two lattice water molecules. The coordination geometry of the 223 central atom Cd (II) with coordinated atoms, and the unit cell of 1, are depicted in Fig. 1(b) 224 and Fig. 1 (c). Both coordinated and free HL ligands, keep their hydrogen atoms, and also the 225 ligands are positively charged through protonation of the nitrogen of the aromatic ring which 226 are in agreement with FT-IR and ¹HNMR data. Interestingly, the six HL ligands are 227 coordinated to Cd(II) center with their oxygen atoms and causes a distorted octahedral geometry around the Cd(II) center. The polyoxoanion $PMo_{12}O_{40}^{3-}$ is a well-known α -Keggin 228 229 structure composed of twelve corner sharing MoO₆ octahedral with the central phosphorus 230 atom coordinated to four oxygen atoms in a distorted tetrahedral fashion. The P-O distances 231 are in the range of 1.520 to 1.543 Å, and O–P–O angles are in the range of 108.9°-110.2°. The 232 Mo–O distances can be classified as follows: Mo–O_t (terminal oxygen) of 1.654–1.714, Mo– 233 Ob-Mo (bridging oxygen) of 1.860-1.963, Mo-Oc-Mo (central oxygen) of 2.406-2.440 234 (Table 2), which are consistent with those described in the literature [38, 40]. The Cd (II) 235 center is bounded to six oxygen atoms of the HL, in a distorted octahedral geometry. The Cd-

O distance as 2.252 - 2.324 Å, is shorter than the corresponding bond length of 2.490(4) Å in 236 $[Cd (HL) (\mu_{11}-N3)_2]_n [48]$. The PMo₁₂O₄³⁻ polyoxoanions, $[Cd(H_2L^+)_6]^{2+}$ cations and isolated 237 238 H_2L^+ molecules are connected with several hydrogen intermolecular interactions into three 239 dimentional (3D) supramolecular structure (Fig. 1(d)). More details about the hydrogen 240 intermolecular interactions for compound 1, are listed in Table 3. The exact role of the lattice 241 water and methanol molecules could not be elucidated because hydrogen atoms of water and 242 OH groups could not be determined from X-ray analysis.

243

3. 3. FT-IR, NMR and UV-Vis spectroscopy

244 The FT-IR spectra of single crystal and nanohybrid 1, were compared with that of the free HL in the region 4000–500 cm⁻¹ as shown in Fig. 2 (A) The weak band v (NH₂) is observed 245 at 3321 cm⁻¹ for HL, and respectively at 3457 and 3460 cm⁻¹ for single crystal and 246 nanohybrid 1. The related band v (N-H) is observed at 3160 cm⁻¹ for HL, and at 3106 cm⁻¹ 247 for both single crystal and nanohybrid. Observation of v(N-H) in the spectra of compound 1 248 249 provides strong evidence for ligand coordination to the Cd(II) center in the keto form [59]. The strong v(C=N) band of HL around 1613 cm⁻¹ is found to be shifted to lower 250 frequencies in 1 and appeared at 1623 cm⁻¹ in the spectrum of compound 1 [48-51]. An out-251 of-plane bending vibrations of the pyridine ring in the free ligand is assigned at 622 cm⁻¹ 252 253 which is disappeared in the single crystal and nanohybrid **1**, is confirmative that the pyridine 254 nitrogen is not coordinated and according to ¹HNMR results pyridine nitrogen is protonated 255 and the ligand HL is in the protonated form H_2L^+ in the structure of nanohybrid 1. Also the 256 difference Fourier of single crystal X-ray diffraction, indicates strongly this possibility. 257 Furthermore, the spectrum of **1** showed four major characteristic vibrations bands, resulting from phosphomolybdic acid with Keggin structure: $v_{(P-Oa)}$, $v_{(Mo-Ot)}$, $v_{(Mo-Oa)}$ and $v_{(Mo-Ob)}$ at 258 259 1080, 980, 890 and 810 cm⁻¹, respectively. By comparing the IR spectrum of the title compound with that of $H_3PMo_{12}O_{40}$.n H_2O (v = 1064 (P–O_a), 963 (Mo–O_t), 867 (Mo–O_a) and 260

782 (Mo–O_b) cm⁻¹ [39,40], red shift appears for the vibration bands of the P–O_a, Mo–O_t and 261 262 Mo–O_a bond, while the vibration bands of the Mo–O_b bond is blue shifted. This demonstrates 263 that the P-Oa, Mo-Ot, Mo-Oa bonds become weaker while the Mo-Ob bond become 264 somewhat stronger in 1. Furthermore, the FT-IR spectra confirms that PMo_{12} cluster in 1, still 265 maintains the basic Keggin structure, in agreement with the single crystal X-ray diffraction 266 analysis. The FT-IR spectra of single crystal and nanohybrid 1, are in a good accordance 267 which confirms the same composition for them. For more details, the HL and single crystals 1, were characterized with ¹³CNMR in (CD₃)₂SO solution (Fig. S1). The ¹³CNMR of HL, 268 269 demonstrate all of the carbon atoms with different environments which are summarized in the synthesis section. The ¹³CNMR spectra of single crystals **1**, demonstrated the same bands 270 271 related to carbon atoms of free HL with a partial chemical shift and also there is a waek band 272 at $\delta = 58$ ppm related to carbon atoms of methanol molecules. The ¹HNMR spectrum of HL and single crystals 1, are shown in Fig. S2. ¹HNMR studies permitted the assignment and 273 quantification of the different ¹H chemical environments for the HL and compound 1. As 274 275 summarized in the synthesis section, all of the characterized bands of hydrogen atoms of HL are observed exactly in the ¹HNMR spectra of compound **1**, with only a minor chemical shift. 276 277 In the spectra of compound **1**, Presence of a band at $\delta = 11.23$ ppm for the NH bond of HL concluded that the HL kept its hydrogen atom. Also a broad band at $\delta = 7.00$ ppm 278 279 demonstrate the nitrogen atoms of the aromatic rings, are protonated. Also comparing the 280 ¹HNMR spectra of HL with single crystals 1, some new bands is observed in the spectra of 281 compound 1. A sharp band at $\delta = 3.15$ ppm related to hydrogen atoms of C—H bonds of 282 methanol molecules and a broad band at $\delta = 4.1$ ppm related to hydrogen atoms of O—H 283 bonds of methanol and water molecules.

The UV-vis spectra of HL, $H_3PMo_{12}O_{40}$ (PMo₁₂) and nanohybrid **1**, were measured in the region of 200 to 500 nm in ethanol solvent (Fig. S3). The HL, shows three absorption bands

at 210, 280 and 300 nm which are associated with $\pi \to \pi^*_{\text{pyridine}}, \pi \to \pi^*_{\text{imine}}$ and $n \to \pi^*_{\text{pyridine}},$ 286 287 respectively. The presence of a sharp absorption band at 220-240 nm in the spectra of PMo₁₂ 288 corresponds to $O_{b/c} \rightarrow Mo$ ligand to metal charge transfer. The UV-vis spectrum of nanohybrid 289 1, has a sharp and obvious band at 220-240 nm corresponding to PMo_{12} in structure of 1. 290 While observation of a shoulder band at 270 nm and a broad band at 290 nm related to HL, 291 confirms the HL the successful synthesis of compound 1. Interestingly, the related bands of 292 HL in the spectra of compound 1, are shifted to lower wavelength which suggests the 293 coordination of HL to the metal centers. The results are in good agreement with similar works 294 reported in the literature [48-51].

295 **3. 4. X-ray Powder Diffraction**

To confirm the phase purity of single crystal and nanohybrid 1, X-ray powder diffraction 296 297 (XRPD) experiments were carried out and the patterns are depicted in Fig. 2 (B). In the XRD 298 patterns of compound 1, three peaks are observed at $2\theta = 10.24^{\circ}$, 12.08° , 14.14° for 299 nanohybrid **1** and at $2\theta = 10.28^{\circ}$, 11.57° , 14.05° for single crystal 1 (Fig. 2B (a) and (b)). 300 Also the experimental XRD patterns, are compared with the corresponding simulated pattern 301 based on the X-ray structure model (Fig. 2B (c). As can see in Fig. 2B, the nanohybrid 1 and 302 the pulverized single crystal 1, have the same XRD profiles. The results suggest good 303 agreement with obtained data and confirm the same composition without any impurity for 304 both nanohybrid and single crystal **1**. The average size of the particles was estimated to be 50 305 nm using the Scherrer formula D= $0.891\lambda / \beta \cos\theta$, where D is the average grain size, λ the 306 X-ray wavelength (1.5418 Å), β the full-width at half maximum of an observed peak and θ its 307 diffraction angle.

308 **3.5. EDX, SEM and BET analysis**

The successful synthesis of nanohybrid **1**, was further verified by the chemical composition analyzed by EDX, which confirmed the presence of C, N, O, P, Mo and Cd

311 elements. According to EDX mapping images of nanohybrid 1 (Fig. S4), these elements are 312 uniformly distributed in 1. The SEM images of nanohybrid material 1 (Fig. 3) reveals plate-313 like morphologies [43] with diameters ranging 200 nm- 1 µm, and thicknesses about 50-100 314 nm. The nitrogen adsorption method was used to determine BET surface area of nanohybrid 315 material **1**. They show type III isotherm (Fig. S5) with the type H3 loop hysteresis according 316 to the IUPAC classification [60-62], indicating the presence of mesopores 2–50 nm. The 317 surface area and total pore volume of nanohybrid 1, are 5.9 nm and 6.16×10^{-3} cc/g, 318 respectively and the average pore diameter are $4.2 \text{ m}^2/\text{g}$.

319 **3. 6. Thermal analysis**

320 Thermogravimetric and differential thermal analysis (TG-DTA) were performed in the 321 range of 40-820°C in static air atmosphere in order to study the behavior of the nanohybrid 322 and single crystal 1 during the heat treatment (see Fig. 4 (a) and (b)). The TG curve of single 323 crystal 1, exhibits three weight loss steps in the range of 40–820 °C. The first weight loss of 324 6.8% (calc. 6.7%) below 200 °C corresponds to the loss of noncoordinated water and 325 methanol molecules. The second and third weight loss of 18.5 % (calc. 19.5%) occurred in 326 the range of 220–560 °C in TG curve which are attributed to the elimination of molecules of 327 organic ligand. Obviously these weight losses, accompanied with three exothermic peaks in the DTA curve. Collapse of $PMo_{12}O_{40}^{3-}$ clusters occurs in the range of 560–820 °C without 328 329 weight loss in TG curve but an endothermic peak is observed in the DTA curve. These results 330 are in good agreement with the structural formula of compound 1, which obtained from 331 single crystal X-ray diffraction. Nanohybrid materials 1, exhibit the weight loss similar to 332 single crystal 1. The DTA curves, have the same general appearance for both nanohybrid and 333 single crystals 1, however, the exo and endothermic peaks have different intensities. 334 Nonetheless, the nanohybrid materials are less stable and their decomposition steps are

shifted about 5-10 °C towards lower temperatures which is in agreement with previous
reports [44,63].

337

338 **3.7.** Adsorption of dyes

339 In this study, the adsorption performances of nanohybrid 1, towards dye pollutants were 340 investigated. Firstly, the nanohybrid 1, was used for removal of different organic dyes such as 341 methylene blue (MB) and rhodamine B (RhB) as cationic dyes and methyl orange (MO) as 342 anionic dye. The UV-vis time dependent absorption spectrum of MB solution under 343 adsorption condition on nanohybrid 1, is depicted in Fig. 4(c) and the related C/C_0 plots 344 versus reaction time for MB and RhB solutions, are shown in Fig. 4(d). The results show that 345 nanohybrid 1, can remove the MB and RhB dyes in short contact time of 5-6 min, with 346 adsorption capacity of 37% and 33%, and removal efficiency of 98% and 86%, respectively. 347 The digital images of MB dye adsorption, clearly shows the color change from blue to 348 colorless solution (see Fig.4(c)). The nanohybrid $\mathbf{1}$, is not efficient for removal of MO dyes 349 (Fig. S6). It suggests that, in this study, the dye removal was mainly achieved by electrostatic 350 interactions between anionic charged nanohybrid 1, and cationic charged MB and RhB dye 351 molecules. In the other words, the nanohybrid 1, and MO dye molecules, both have anionic 352 charge and repel each other, as a result, there is neither electrostatic interaction nor adsorption 353 property between the nanohybrid **1** and MO molecules. Furthermore the observed difference 354 in removal efficiency of nanohybrid 1, towards MB and RhB, is originated from this fact that, 355 the RhB is a dye with large molecules in contrast with MB and this causing a steric hindrance 356 between the RhB molecules and the active adsorption sites on nanohybrid 1, and lead to 357 slower removal of RhB in contrast with MB [64,65].

For investigate the best condition for removal of MB molecules, with nanohybrid **1**, several experiments were carry out by altering other variables, including the different dosage of adsorbent **1**, different concentration of MB and different pH values.

361 The Fig. 5(a) and (b), show the effects of adsorbent dosage on the removal of MB. 362 Furthermore for more details, the related UV-vis time dependent absorption spectrum of MB 363 on nanohybrid 1, are depicted in Fig. S7. Along with the increase of adsorbent dosage from 364 15 mg/L to 30 and 45 mg/L, the removal of MB shows a significant increasing trend and the 365 time of adsorption, decreases from 7 to 5 and 4 min with removal efficiency of 98%. As can 366 see in Fig. 5 (a), the adsorption capacities decreases from 73 to 37 and 20.8 for 15, 30 and 45 367 mg/L dosage of adsorbent 1. The reason can be described that by increasing the dosage of 368 adsorbent in the same volume of MB solution (50 mL), there are not enough MB molecules 369 for generating driving force to overcome the mass transfer resistance of the dye and the 370 adsorbent are dispersed in dilute MB concentrations and the adsorption process has reached 371 equilibrium in short time [66]

372 Effects of initial MB concentrations (25, 35 and 45 mg/L) on adsorption performance was 373 evaluated and the results are shown in Fig. 5(c) and (d). The UV-vis time dependent 374 absorption spectrum are depicted in Fig. S8. Along with increasing the initial MB 375 concentrations, the adsorption performance completed in long time. Interestingly as can see 376 in Fig. 5. (d), by increasing the initial MB concentrations from 25 to 35 and 45 mg/L, the 377 adsorption time increased from 5 min to 9 and 45 min while the removal efficiency is same as 378 98%, 97% and 97% respectively. The equilibrium adsorption capacity (37.5 mg/g) at initial 379 MB concentration of 25 mg/L increase to adsorption capacities of 49.3 and 62 mg/g at the 380 concentration of 35 and 45 mg/L of MB solutions. As can see in Fig. 5 (c), with increasing 381 the initial concentration of MB, the adsorption capacities increase and then keep constant at a 382 slow speed. The results can be ascribed to the fact that, most vacant surface sites are available

for the adsorption at the initial stage. However, with the adsorption progressing, the available surface sites become less, and harder to be utilized due to repulsive forces between the MB molecules adsorbed onto adsorbent **1** and bulk phase [66-68]. In fact by increasing the concentration of MB, the driving force is increase and lead to higher adsorption capacities.

387 The initial solution pH, has been identified as a rather significant variable enhancing or 388 depressing the adsorption capacity of adsorbate molecules, which is attributed to influencing 389 surface binding sites or charges of the adsorbent [66,67]. The effect of initial solution pH on 390 MB adsorption onto nanohybrid 1, was investigated in the pH range from 2 to 10. Fig. S9 391 shows the UV-vis time dependent absorption spectrum of MB solution in different pH values. 392 The related qt/t and R/t plots are depicted in Fig. 5(e) and (f) respectively. From the results 393 shown in Fig. 5(f), it observed that by increasing initial pH of MB from 2 to 10, the removal 394 efficiency decrease from 99% to 65% while the adsorption capacities increased from 33.5 at 395 pH = 2 to 35.2 at pH = 4 and to 37.5 at pH = 6 and then the adsorption capacities decrease to 30 396 and 28.5 at pH=8 and 10, respectively. Also, according to results depicted in Fig. S9, the 397 adsorption time is increased from 5 min at pH=6 to 8 and 12 min at pHs 8 and 10 respectively 398 while decrease to 2 and 5 min for acidic solutions with pH 4 and 2, respectively. Moreover, 399 it is obvious that the adsorption capacity and removal rate can reach 33.5 mg/g and 99% at 400 low pH, further suggesting that acidic solutions benefited MB adsorption. This phenomenon 401 can be explained that POMs with highly electronegative possessed a good adsorption towards 402 the cationic dyes [66]. With increasing the initial pH from 6, the adsorption capacity and 403 removal efficiency were decrease. It can be related to this observation that, the chloride anion 404 in MB was exchanged with NaOH to have a displacement reaction, forming NaCl (aq) and 405 MBS ⁺ OH (aq). However, the salt of NaCl might result in the deactivation of nanohybrid 1, 406 and decrease the adsorption of $MBS^+ OH$ (aq) on it [66, 68].

407 The stability and reusability of adsorbent material, is an important factor for its practical 408 applications. When the adsorption process was over, the adsorbent sample saturated with dye 409 molecules, were separated by centrifugation due to its insolubility in water, washed with 410 water and ethanol several times and dried overnight at 70 °C and reused for adsorption again. 411 The adsorption processes were repeated for three times. Each run is carried out under the 412 same condition. As can see in Fig. 5. (g), there is a partial decrease in the removal efficiency 413 of the adsorbent 1, at the third cycle, with removal efficiency of 96% towards MB and 83% 414 towards RhB. Moreover, the FT-IR spectrum of nanohybrid 1, after three cycles of use, is 415 shown in Fig. 2A (d). It confirms that, the structure of nanohybrid 1, remains intact without 416 losing its adsorption efficiency over three cycles of adsorption experiments. The results 417 suggest the nanohybrid **1**, as an efficient and reusable adsorbent to removal of cationic dyes.

418

419 **4.** Conclusions

420 In summary, a new polyoxometalate based nanohybrid material with Cd (II) semicarbazone 421 complex, $[Cd(H_2L^+)_6][H_2L^+]_4[PMo_{12}O_{40}]_4.18CH_3OH.4H_2O$ (1), was prepared by a 422 sonochemical route and characterized fully. Also the single crystal 1, were synthesized with 423 branched tube method and used for single-crystal X-ray diffraction analysis. The FT-IR and 424 XRD results are in good agreement and confirm the same composition for it. The nanohybrid 425 material 1, was used for removal of different organic dyes from aqueous solutions. The 426 results reveal that, 1, can remove the cationic dyes with very good efficiency but it is not 427 effective for removal of anionic dyes. These results are correlated with the presence of PMo₁₂O₄³⁻ polyanions in the structure of **1**. The nanohybrid **1**, can adsorb MB and RhB 428 429 molecules in short time of 5 and 6 min with removal efficiency of 98% and 86% respectively. 430 Furthermore, the nanohybrid 1, can be readily recycled several times without significant loss 431 of its adsorption activity.

432

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438 Appendix A. Supplementary data

439 Crystallographic data (excluding structure factors) for the structure reported in this paper 440 have been deposited with the Cambridge Crystallographic Data Centre as supplementary 441 publication no. CCDC as 1448105. Copies of these data can be obtained free of charge on 442 application to CCDC, 12 Union Road, Cambridge CB2 2EZ, UK; FAX: (+44) 1223 336033, 443 or online via www.ccdc.cam.ac.uk/data_request/cif or by emailing 444 data_request@ccdc.cam.ac.uk.

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	Chemical Formula	$C_{88}H_{106}C_{0}M_{1048}N_{40}O_{192}P_{4}$
	Formula weight	9637.3
	Radiation type	Μο Κα
	Crystal size (mm)	0.49 imes 0.32 imes 0.20
	Temperature (K)	120
	Crystal system	Triclinic
	Space group	P -1
	a (Å)	13.2377(2)
	b (Å)	19.5954(3)
	c (Å)	25.4879(4)
	α (°)	98.7446(13)
	β(°)	94.6958(14)
	γ(°)	102.4346(14)
	Volume (Å ³)	6336.23(18)
	Z	1
	ρ calculated (g cm ⁻³)	2.532
	μ (mm ⁻¹)	2.51
	$T \min, T \max$	0.772, 1
	R(reflections)	0.0587(24832)
	wR2 (reflections)	0.0811(28898)
Ć	$\Delta ho_{\rm max}, \Delta ho_{\rm min} ({ m e} { m \AA}^{-3})$	4.75, -5.11
<i>r</i>		

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Table 2. Selected bond lengths (Å) and angles (deg) for compound 1

Cd1—O32	2.324 (5)	O32—Cd1—O32i	180.0 (5)
Cd1—O32 ⁱ	2.324 (5)	O32—Cd1—O33	86.4 (2)
Cd1—O33	2.276 (7)	O32—Cd1—O33i	93.6 (2)
Cd1- O33 ⁱ	2.276 (7)	O32—Cd1— O57	94.7 (2)
Cd1 057	2.252 (6)	O32—Cd1—O57i	85.3 (2)
Cd1- O57 ⁱ	2.252 (6)	O33—Cd1—O33i	180.0 (5)
P1	1.528 (6)	O33—Cd1—O57	86.8 (2)
P1	1.547 (6)	O33—Cd1—O57i	93.2 (2)
P1	1.535 (5)	O33i—Cd1—O57	93.2 (2)
P1	1.535 (5)	O33i—Cd1—O57i	86.8 (2)
P2076	1.543 (5)	O57—Cd1—O57i	180.0 (5)
P2077	1.535 (6)	O69—P1—O85	110.2 (3)
P2	1.537 (6)	O69—P1—O89	109.4 (3)
P2	1.520 (5)	O69—P1—O91	110.2 (3)
O32—C23	1.268 (11)	O89—P1—O91	109.3 (3)
O33—C25	1.243 (11)	O76—P2—O77	109.3 (3)
O57—C42	1.237 (11)	O76—P2—O92	109.6 (3)
O19—C21	1.280 (14)	O77—P2—O87	109.5 (3)
O12—C16	1.267 (11)	O87—P2—O92	108.9 (3)
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695	Table 3. Selected hydrogen bonding parameters (Å, °) for compound 1
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D—H····A	D—H	Н…А	D····A	D—H····A	
С1—Н1…О27	0.96	1.88	2.809 (8)	161.18	
C1—H1…N1	0.96	2.35	2.706 (10)	101.44	
С22—Н16…О13іі	0.96	2.31	3.255 (12)	168.31	
C22—H17…O45iii	0.96	2.39	3.215 (14)	144.21	
С26—Н19…О25	0.96	2.44	3.217 (13)	138.34	
С32—Н25…О9ііі	0.96	2.44	3.105 (13)	126.21	
C36—H31…O17iv	0.96	2.44	3.392 (9)	171.31	

Symmetry codes: (ii) -x, -y+1, -z; (iii) x, y+1, z; (iv) -x+1, -y, -z.



Fig. 1. (a) The symmetric unit of $[Cd (H_2L^+)_6][H_2L^+]_4[PMo_{12}O_{40}]_4.18CH_3OH.4H_2O$ (1), (b) coordination geometry around central atom Cd (II), (c) View of the unit cell of 1 in the direction of the crystallographic b axis and (d) packing representation of compound 1.

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Fig. 2 (A) The FT IR spectra of : (a) HL ligand, (b) nanohybrid material 1, (c) single crystal 1, (d) nanohybrid
material 1 after adsorption experiments; and (B): PXRD patterns of (a) nanohybrid material 1, (b) single crystal
1 and (c) simulated pattern from single crystal X-ray data of compound 1.







Fig. 3. (a)-(d) FESEM photographs of nanohybrid material (1) at different magnifications.



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780 Fig. 4. (a) TG-DTA of nanohybrid material 1, (b) TG-DTA of single crystal 1, (c) The adsorption rate of MB 781 over nanohybrid 1. The inset photo shows the color change of MB solution with time of adsorption, and (b) Plot 782 of C/C_0 against time for MB and RhB over nanohybrid 1.



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Fig. 5. The effect of adsorbent dosage on: (a) adsorption capacity and (b) Removal rate; Effect of initial
concentration of MB solution on: (c) adsorption capability and (d) Removal rate; Effect of initial pH of MB
solution on: (e) adsorption capability and (f) Removal rate; and (g) The recyclability tests

Highlights

- A new nanohybrid containing Cd(II) semicarbazone and $PMo_{12}O_{40}^{3-}$ was synthesized.
- This nanohybrid revealed a 3D supramolecular structure via hydrogen interactions.
- This nanohybrid was tested as an adsorbent for the removal of dye pollutants.
- The results showed that the nanohybrid is an excellent adsorbent for cationic dyes.
- The nanohybrid can be easily separated and reused without the loss of ability.