

Huge Deuterated Effect on Permittivity in a Metal–Organic Framework

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Abstract: Colorless block crystals of MOF (metal-organic framework) **1** and **2** were prepared in respective yields of 65 and 60% by thermal treatment of HQA (HQA = 6-methoxyl-(8*S*,9*R*)-cinchonon-9-ol-3-carboxylic acid) with ZnBr₂ in either H₂O or D₂O and 2-butanol at 70 °C for 1–2 days. The MOFs **1** and **2** are isostructural, one-dimensional chains in which the local coordination geometry around the Zn center can be best described as a slightly distorted tetrahedron defined by two bromine atoms, one nitrogen atom of quinoline from HQA, and an oxygen atom of carboxylate from HQA. The

nitrogen atom of the quinuclidine of HQA is protonated in a zwitterionic form. The MOFs **1** and **2** crystallize in a polar point group (*C*₂, space group *P*2₁) which belongs to ferroelectric active compounds. MOFs **1** and **2** display both ferroelectric behavior and large dielectric constants. Interestingly, at low frequency range the dielectric response to water can achieve an approximate increase of more than

600%. Crystal parameters: **1**: C₂₀H₂₈Br₂NO₇Zn, *M* = 619.62, monoclinic, *P*2₁, *a* = 9.5711(8), *b* = 12.0486(10), *c* = 11.1972(9) Å, *α* = *γ* = 90, *β* = 98.4(2)°, *V* = 1277.39(18) Å³, *Z* = 2, *ρ*_{calcd} = 1.611 mg m⁻³, *R*₁ = 0.0499, *wR*₂ = 0.0982, *μ* = 4.126 mm⁻¹, *S* = 1.015, Flack value = 0.032(13); **2**: C₂₀H₂₂D₆Br₂NO₇Zn, *M* = 625.66, monoclinic, *P*2₁, *a* = 9.5650(9), *b* = 12.0392(11), *c* = 11.1973(10) Å, *α* = *γ* = 90, *β* = 98.44(2)°, *V* = 1275.5(2) Å³, *Z* = 2, *ρ*_{calcd} = 1.629 mg m⁻³, *R*₁ = 0.0543, *wR*₂ = 0.1072, *μ* = 4.133 mm⁻¹, *S* = 1.056, Flack value = 0.025(17).

Keywords: dielectric response • ferroelectricity • isotope effects • metal–organic frameworks • zinc

A striking common feature of all ferroelectric and permittivity H-bonded pure organic and inorganic compounds is undoubtedly the huge isotope effect observed upon deuteration.^[1] A notable example in pure inorganic compounds is KD₂PO₄ (DKDP) which has been shown to exhibit saturation spontaneous polarization *P*_s and permittivity (*ε*_i) values of ≈ 24% and 80%, respectively, higher than those for KDP (KH₂PO₄).^[2] Huge isotope effects have also been reported for pure organic systems, and notable examples in this area have included works by the groups of Horiuchi^[3] and Suga-

wara^[4] who showed that a temperature increase of 50 °C in samples of phenylsquaric acid (both the protonated Phz-H₂ca; Phz = phenazine, H₂ca = bromanilic acid and deuterated Phz-D₂ca) could produce a significant observed increase in the dielectric deuterated effect (DEF) from 8 to 18 times, respectively. Such giant effects were first explained by a quantum tunneling model that postulated that individual protons had the ability to tunnel between wells in single-proton double wells. In view of the fact protons are more delocalized than deuterons, it was suggested that this made the onset of the disordered paraelectric phase more favorable.^[2] As a consequence, DEF has become an attractive and convenient strategy to enhance the physical properties of materials associated with noncentrosymmetric space groups, such as second-harmonic generation (SHG), ferroelectricity, and permittivity (ferroelectric relaxation). To our knowledge, however, studies on DEF in metal-organic framework (MOF) systems have remained rare, which is surprising since such materials can potentially mimic the useful properties found in both organic and inorganic compounds. Recent works have demonstrated MOFs to be useful materials in numerous applications that include gaseous storage, catalysis, separation, and molecular recognition.^[5] In this context

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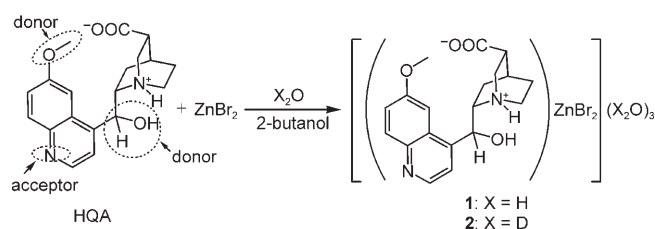
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and as part of an ongoing program in our laboratory to explore the scope of homochiral MOFs as SHG, ferroelectric, and dielectric materials.^[6] We report herein the synthesis, crystal structure, SHG response, ferroelectricity, and dielectric properties of 1D homochiral MOFs $[\text{Zn}(\text{HQA})\text{Br}_2(\text{H}_2\text{O})_3]_n$ (**1**: HQA = 6-methoxy-(8*S*,9*R*)-cinchonan-9-ol-3-carboxylic acid^[7]) and $[\text{Zn}(\text{HQA})\text{Br}_2(\text{D}_2\text{O})_3]_n$ (**2**). The notable features of these novel MOF systems are: 1) both **1** and **2** crystallize in chiral space group $P2_1$ (point group: C_2) which belongs to one of the 10 polar point groups (C_1 , C_s , C_2 , C_2v , C_3 , C_3v , C_4 , C_4v , C_6 , C_6v) associated with SHG response and ferroelectricity, and 2) detection of a huge DEF ($\approx 625\%$ increase) on permittivity (ϵ_r) following deuterium substitution (from **1** to **2**) which, to our knowledge, has not been previously reported for MOF systems.

Colorless block crystals of MOFs **1** and **2** were prepared in respective yields of 65 and 60% by thermal treatment of HQA with ZnBr_2 in either H_2O or D_2O and 2-butanol at 70°C for 1–2 days, as shown in Scheme 1. The evidence for



Scheme 1.

product formation was based on elemental analyses and IR spectroscopic measurements. The IR revealed a strong peak at $\tilde{\nu} = 1621\text{ cm}^{-1}$ and two medium peaks at $\tilde{\nu} = 1470$ and 1394 cm^{-1} , which can be attributed to the $\tilde{\nu}(\text{CO})$ stretch of the carboxylate group. A broad peak at $\tilde{\nu} = 3455\text{ cm}^{-1}$ for **1** and a weak peak at $\tilde{\nu} = 2440\text{ cm}^{-1}$ (see Supporting Information) for **2** suggests the presence of H_2O and D_2O molecules in these MOF systems, and that the N atom of the quinuclidine ring is protonated. This in turn implies that the HQA ligand exists in its zwitterionic form in **1** and **2**, which is not be surprising given that the ligand is a β -amino acid. In this context, it might be expected that the 6-methoxyquinoline ligand would be a good donor–acceptor (pyridyl group as acceptor) system, which is an essential feature for SHG response. The HQA ligand can be considered to be charge separated and a good donor–acceptor chromophore (see Scheme 1).

X-ray single crystal structural determination^[13] of **1** reveals that the local coordination geometry around the Zn center can be best described as a slightly distorted tetrahedron composed of two terminal Br^- ions, an oxygen atom from the carboxylate group, and a nitrogen atom from the quinoline ring (Figure 1, top).^[8] Each HQA can be considered as a bidentate spacer that links two Zn centers together to furnish a 1D wave-like chain (Figure 1, bottom). The dipolar moment (μ_1 , pink arrow) along each chain can be con-

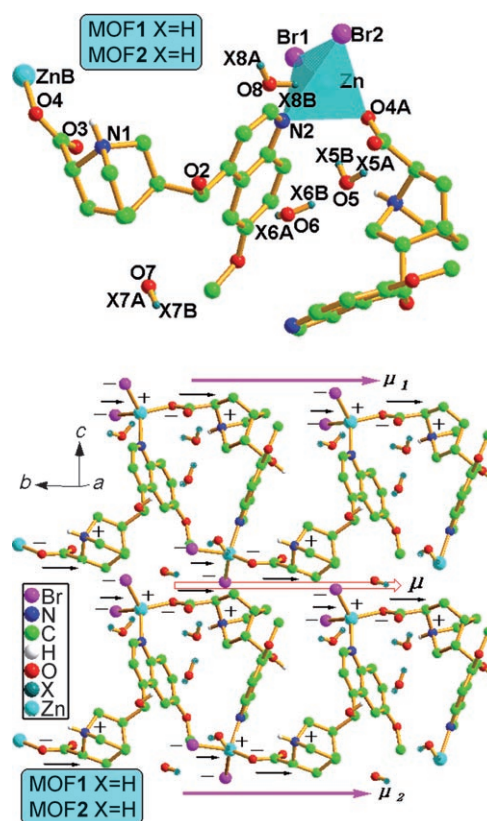


Figure 1. The asymmetric unit representation of **1** and **2** in which the local coordination geometry around Zn center is described as a slightly distorted tetrahedron (top). Two chains representation of **1** and **2**, in which each chain dipolar moment (μ_1 and μ_2 , pink arrows) are in the same direction and strengthening of the total dipolar moment (μ), which cannot be cancelled (bottom).

sidered with the negative and positive charges sitting on the oxygen atom of carboxylate group and N atom of quinuclidine ring, or N1 and Zn atoms respectively, and a small dipolar moment (dark arrow) between these atoms. This means that each chain dipolar moment (μ_1 and μ_2) is always moving in the same direction, thus strengthening the total dipolar moment (μ , yellow arrow) within the chains and, therefore, cannot be cancelled. The presence of numerous H-bonding interactions (see Supporting Information) in **1** results in the formation of a H-bonded 3D framework (Figure 2). MOFs **1** and **2** are also isostructural with respect to each other.

In this work, the SHG response of **1** and **2** were examined since both MOFs crystallized in the chiral space group $P2_1$, as mentioned earlier. Owing to the absence of absorption peaks beyond $\lambda = 350\text{ nm}$ in the UV-vis spectra of **1** and **2**, and phase-matchability (see Supporting Information), our preliminary findings reveal that the respective estimated SHG responses for **1** and **2** are 18 and 22 times larger than that for KDP. The difference in the approximate estimations in our MOF systems indicates that there is a slight DEF on SHG response observed in our experiment. We attribute the

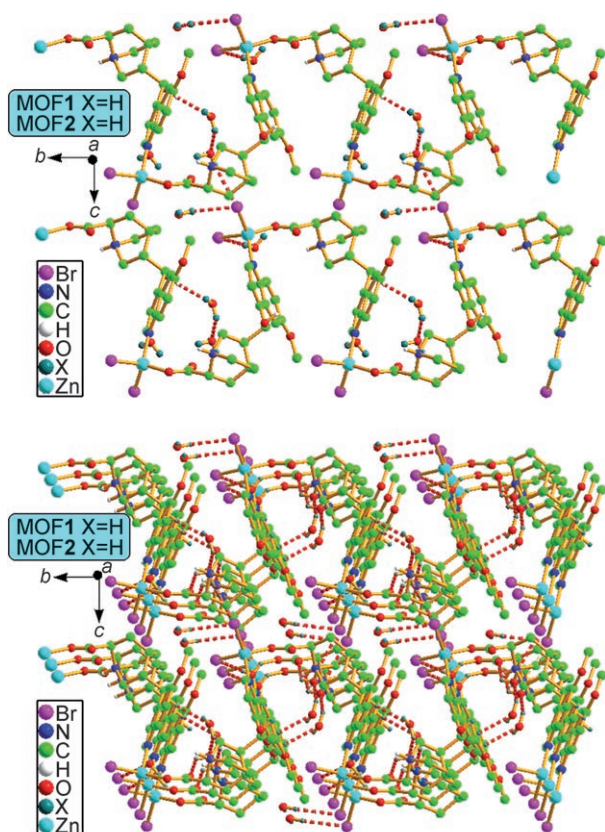


Figure 2. Perspective views of: The 2D framework of **1** and **2** through H-bonding along the *a*-axis (top); the 3D framework of **1** and **2** through H-bonding along the *a*-axis (bottom).

strong SHG response to be due to the presence of the zwitterionic moiety, the inclusion of which is a strategy commonly employed to enhance nonlinear optical properties.^[9]

As depicted in Figure 3 (top), pellets of powdered samples of **1** and **2** clearly show that both MOFs exhibit typical ferroelectric behavior (hysteresis loop, ferroelectric measurements on single crystals of **1** and **2** further confirm that both MOF do indeed display ferroelectric properties (see Figures S4-1 in the Supporting Information), and display a remnant polarization (P_r) of $\approx 0.16 \mu\text{Ccm}^{-2}$ for **1** and $0.17 \mu\text{Ccm}^{-2}$ for **2**. Saturation of the spontaneous polarizations (P_s) in **1** and **2** occur at ≈ 0.30 and $0.34 \mu\text{Ccm}^{-2}$, respectively, which are slightly larger than that for a typical ferroelectric compound (e.g. $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$, Rochelle salt; usually $P_s = 0.25 \mu\text{Ccm}^{-2}$), but significantly smaller than that found in KDP ($\approx 5 \mu\text{Ccm}^{-2}$). This suggests that there is a slight ferroelectric DEF (with an increase in the P_s value of 13%) $[(0.34 - 0.30)/0.30]$ detected on going from **1** to **2**. However, by assuming one dipole in the unit cell ($Z=2$) contains two *DA* pairs (the density of dipoles, $N_1 = Z/V_{\text{cell}} = 1.5657 \times 10^{27} \text{ m}^{-3}$ for **1**) it should be noted that the cubic moment $\mu_s = P_s/N_1 = 1.916 \times 10^{-30} \text{ Cm} \approx 0.57$ Debye (calculated from the saturated polarization $P_s = 0.30 \mu\text{Ccm}^{-2}$ at 298 K, derived by extrapolation of the hysteresis loops plotted in Figure 3, top). Similarly, N_2 is equal to $Z/V_{\text{cell}} = 1.568 \times$

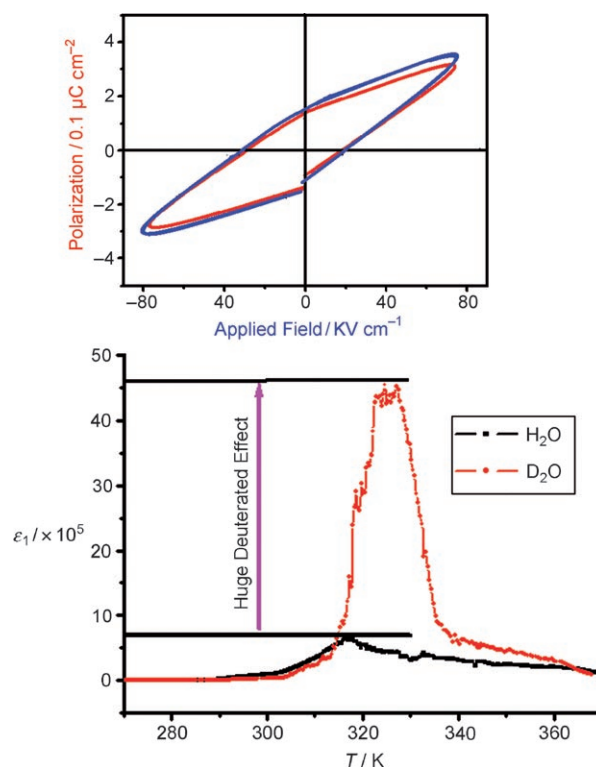


Figure 3. Electric hysteresis loops of powdered samples in the form of pellets of **1** (red line) and **2** (blue line) observed by Virtual Ground Mode in a using an RT6000 ferroelectric tester at room temperature (top). Temperature dependence of the real parts (ϵ_1) of the dielectric response of **1** (dark line) and **2** (red line) at 1k Hz (bottom).

10^{27} m^{-3} for **2** and μ_s is equal to $P_s/N_2 = 2.168 \times 10^{-30} \text{ Cm} \approx 0.65$ Debye, which is slightly larger than that of **1** and thus, supports the view that the SHG response of **1** is slightly weaker than that of **2**.

The temperature dependence of the ac dielectric permittivity of powdered samples of hydrated **1** and deuterated **2** in the form of pellets were measured on an HP4191A Analyzer over the temperature and frequency range of 77–373 K and 100 Hz to 1 MHz, respectively (Figure 3, bottom). The permittivity (ϵ_1) ($\epsilon = \epsilon_1 - i\epsilon_2$) of **1** reaches a maximum value of 4.5×10^5 at a temperature of ≈ 317 K, while the permittivity of **2** reaches a maximum value of 6.2×10^6 at ≈ 325 K. This allows the dielectric DEF at the lowest frequency of 1 kHz to be estimated to be equal to 626%. However, the temperature DEF is not evident with an observed increase of only 8 K. As the frequency is increased from $10^3 \rightarrow 10^{3.5} \rightarrow 10^4 \rightarrow 10^{4.5} \rightarrow 10^5$ Hz, the dielectric DEF remains constant at $\approx 600\%$ of that observed for **1** (see the Supporting Information). In addition, a continuous increase in the frequencies results in a gradual decrease in permittivity (ϵ_1) which disappears at the highest frequencies. It is noteworthy to mention that this unusual phenomenon has not been observed in either pure organic or inorganic compounds. In addition, a ≈ 10 -fold drop in permittivity with increasing frequencies differs significantly to that for relaxation ferroelectric metal-organic frameworks (sharp drop of 10^2). This suggests that

the ferroelectric behavior could be the result of the presence of extensive H-bonding rather than relaxation ferroelectrics or weak dipole-dipole interactions (generated by either the zwitterionic moiety or distorted tetrahedron geometry of the Zn complex) which results in the huge dielectric response, and would also be in good agreement with the cubic moment values mentioned earlier.^[10] The giant dielectric permittivity (real part; ϵ_1) response could be a result of H-bonding generated by water or deuterated water given that the polarity of water or deuterium oxide can significantly influence dielectric permittivity, particularly at low frequency. A similar phenomenon has been previously reported by Kobayashi and co-workers^[6b] who disclosed that the polarizability of guest molecules such as water and methanol play a vital role in generating giant dielectric constant responses, and a sharp increase from 5 to 20, with an increase of 300% could be accomplished between frameworks with and without guest molecules. In this work, our dielectric permittivity measurements of **1** and **2** reveal a strong peak with $\epsilon_1 \approx 4.5 \times 10^5$ and 6.2×10^6 respectively, at 320 K. In contrast, measurements on the corresponding frameworks without water or deuterium oxide showed that these peaks are replaced by a much weaker peak with $\epsilon_1 \approx 2.3 \times 10^2$ at 300 K. While the possibility that the DEF in water could be a result of a depletion of proton probability density at the O-H-O bridge center, weakening its proton-mediated covalent bonding.^[11] This difference in measurements would, nonetheless, further support the hypothesis that H-bonding in water or deuterium oxide is responsible for the observed giant dielectric response (see the Supporting Information). On the other hand, the possibility that a phase-transition is the cause for the observed giant dielectric permittivity peak at ≈ 320 K is thought to be unlikely, owing to the fact that the water or deuterium oxide molecule only escapes from the framework at their respective boiling point temperatures of 100 and 101.42 °C. In this work, we surmise that the observed phenomenon to result from structural fluctuation of the 3D framework at ≈ 50 °C that is generated through H-bonding during partial elimination of the solvent molecules, particularly given that D₂O is reasoned to be the most likely cause for the huge isotope effect observed in **1** and **2**. The elimination temperatures for H₂O and D₂O from the crystals are also consistent with the dielectric anomalies, which reach a maximum at ≈ 50 °C and imply that the dielectric giant responses are probably a result of the elimination of H₂O and D₂O. This is further supported by measurements on dehydrated MOFs, or MOFs without D₂O, that revealed the huge isotope effect to essentially disappear (Figure S9 in the Supporting Information). It is worth highlighting that similar behavior for the [Mn₃(HCOO)₆(H₂O)(CH₃OH)] framework has been previously reported in which dielectric anomalies at the bulk liquid \leftrightarrow solid transition temperature were noted not to display structural phase-transition presumably, because such systems with a strong 1D nature generally do not exhibiting such phase-transitions.^[6b] On the other hand, there is enhancement of the positional freedom of water (or deuterated water) with the larger polarizability, at around

the onset temperature of weight loss in the TGA measurement that results in the huge dielectric response, which is similar to those MOFs reported by Kobayashi and co-workers.^[6b]

The dielectric permittivity measurements on single crystal mode further confirms the fact that below 300 K temperature range the dielectric deuterated effect exists, reaching 10% (see Figure S10 in the Supporting Information) while the huge dielectric anomaly, on hydrated and deuterated MOF **1** and **2** at around 320 K, is probably a result of the partial loss of polar water and deuterated oxide, the dielectric giant response, and the deuterated effect, particularly at the low frequency range.

At close to room temperature, the static dielectric constants of **1** and **2** (frequency = 0 Hz, estimated from the real part ϵ_1 of frequency-dependent complex dielectric function by extrapolation, the dotted line, of plots depicted in Figure S5 and S6 in Supporting Information) are 362 and 485, respectively.^[12] To our knowledge, such a giant dielectric constant for a MOF-based material is unprecedented.

Conclusion

In the present work, we have demonstrated that dielectric deuterated effect (DEF) can be employed as a strategy to enhance the second-harmonic generation (SHG) response and ferroelectric properties of metal-organic frameworks (MOFs). In particular, we have showed that a huge DEF on permittivity (ϵ_1) in a MOF-based material can be accomplished. This class of materials provides a new impetus to construction of novel functional MOFs with potentially useful physical properties.

Experimental Section

Synthesis of 1: Thermal treatment of ZnBr₂ (1 mmol) and HQA (6-methoxy-(8*S*,9*R*)-cinchonan-9-ol-3-carboxylic acid) (1 mmol) in 2-butanol (1 mL) and H₂O (2–3 mL) at 70 °C over 1–2 days gave beautiful colorless block crystals of **1** in 65% yield based on the amount of HQA consumed, in which only one pure phase on the wall of the Pyrex tube was found. IR (KBr): $\tilde{\nu} = 3454.7(\text{br, s}), 3042.6(\text{m}), 2960.2(\text{m}), 2839.7(\text{m}), 2687.5(\text{m}), 1949.0(\text{w}), 1620.7(\text{s}), 1815.6(\text{s}), 1470.2(\text{m}), 1435.4(\text{m}), 1394.0(\text{s}), 1344.1(\text{m}), 1319.7(\text{m}), 1277.9(\text{s}), 1249.8(\text{s}), 1178.9(\text{w}), 1156.5(\text{w}), 1109.2(\text{m}), 1029.2(\text{m}), 986.3(\text{w}), 956.9(\text{w}), 832.7(\text{m}), 767.6(\text{w}), 650.1 \text{ cm}^{-1}(\text{w})$; elemental analysis calcd (%) for C₂₀H₂₈Br₂NO₇Zn: C 38.73, H 4.52, N 2.26; found: C 38.61, H 4.39, N 2.12.

Synthesis of 2: Following the same procedure as the synthesis of **1**, except that H₂O is replaced by D₂O. This afforded **2** as a colorless block crystals in 60% yield based on the amount of HQA consumed. IR (KBr): $\tilde{\nu} = 3449.5(\text{br, s}), 3039.4(\text{m}), 2961.5(\text{m}), 2838.8(\text{m}), 2685.8(\text{m}), 2440(\text{w}), 1947.5(\text{w}), 1620.7(\text{s}), 1818.2(\text{s}), 1470.3(\text{m}), 1433.9(\text{m}), 1394.4(\text{s}), 1344.2(\text{m}), 1319.7(\text{m}), 1277.4(\text{s}), 1249.7(\text{s}), 1180.4(\text{w}), 1136.6(\text{w}), 1107.5(\text{m}), 1029.2(\text{m}), 986.0(\text{w}), 956.8(\text{w}), 832.6(\text{m}), 767.6(\text{w}), 649.31 \text{ cm}^{-1}(\text{w})$; elemental analysis calcd (%) for C₂₀H₂₂D₆Br₂NO₇Zn: C 38.36, H 3.52, N 2.24; found: C 38.48, H 3.59, N 2.29.

Measurement of SHG response: Approximate estimations of the second order nonlinear optical intensity were obtained by comparison of the results obtained from powdered samples (80–150 μm diameter) in the form

of a pellet (Kurtz powder test^[14]), with that obtained for KDP. A pulsed Q-switched Nd:YAG laser at $\lambda = 1064$ nm was used to generate the SHG signal. The backward scattered SHG light was collected using a spherical concave mirror and passed through a filter that transmits only 532 nm radiation. The SHG responses of **1** and **2** are about 18 and 22 times than that of KDP, respectively. The estimated phase-matching results are listed in Table 1.

Table 1. Estimated powdered phase-matching of particle size vs. SHG intensity

Particle size [μm]	35	55	75	82
SHG intensity (KDP for 1)	18	19	20	21
SHG intensity (KDP for 2)	22	23	24	25

Measurement of electric hysteresis loop: The ferroelectric properties of solid state samples are measured from a powdered sample in form of a pellet using a standard RT 6000 ferroelectric tester (Radiant Technologies, Albuquerque, USA) at room temperature, while sample was immersed in insulating oil, the electric hysteresis loop was observed by Virtual Ground Mode (The measurement is ac, the frequency is ≈ 5 –10 Hz).

Measurement of permittivity: This was conducted using an automatic impedance HP4191 A Analyzer with frequencies of 100 Hz to 1 MHz.^[15]

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