

ESI document

The *in-situ* formation of platinum nanoparticles and their catalytic role in electroactive phase formation in poly(vinylidene fluoride): A simple preparation of multifunctional poly(vinylidene fluoride) films doped with platinum nanoparticles

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Methodology

The systematic study of the Pt-NPs doped PVDF films has been made by preparing the films under different concentration (0.025, 0.25, 0.50, 0.75, 1.0, 1.25 and 1.50 wt%) of Pt-salt in PVDF-DMF solutions. The preparation method and indexing of the free standing films are same as mentioned in the main article.

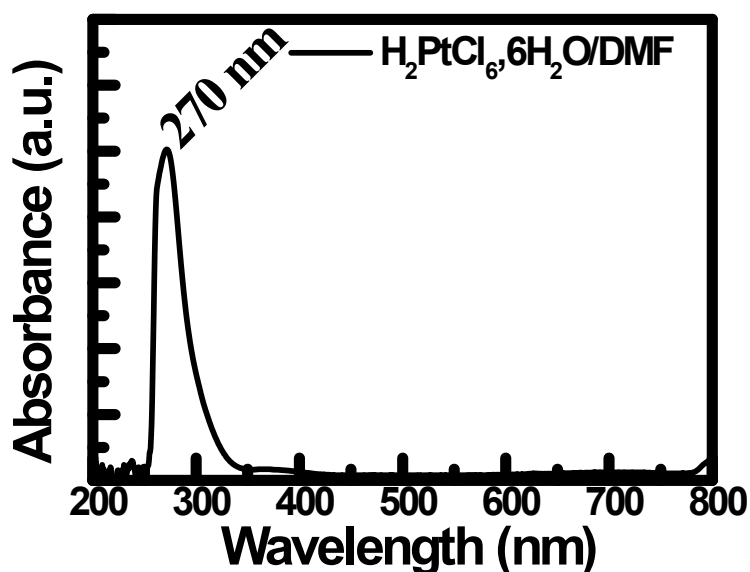
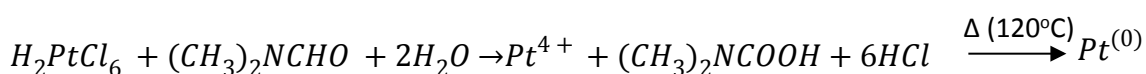


Figure S1. UV-Vis spectra of Pt-salt containing DMF solution.

This spectrum entertains the fact that H₂PtCl₆.6H₂O / DMF solution shows no considerable absorption from visible to ultraviolet region except for an abrupt strong absorption at 270 nm due to the ligand-to-metal charge-transfer transition of the [PtCl₆]²⁻ ions (*i.e.*, due to the presence of Pt⁴⁺ ions in the solution ; [PtCl₆]²⁻ ⇌ Pt⁴⁺ + 6Cl⁻) which is not found in Pt-NPs doped PVDF films. Moreover, the formation of Pt-NPs usually take place while drying of the casted solution, *i.e.*, during the film formation. The proposed chemical reaction involved in this process is as follows:



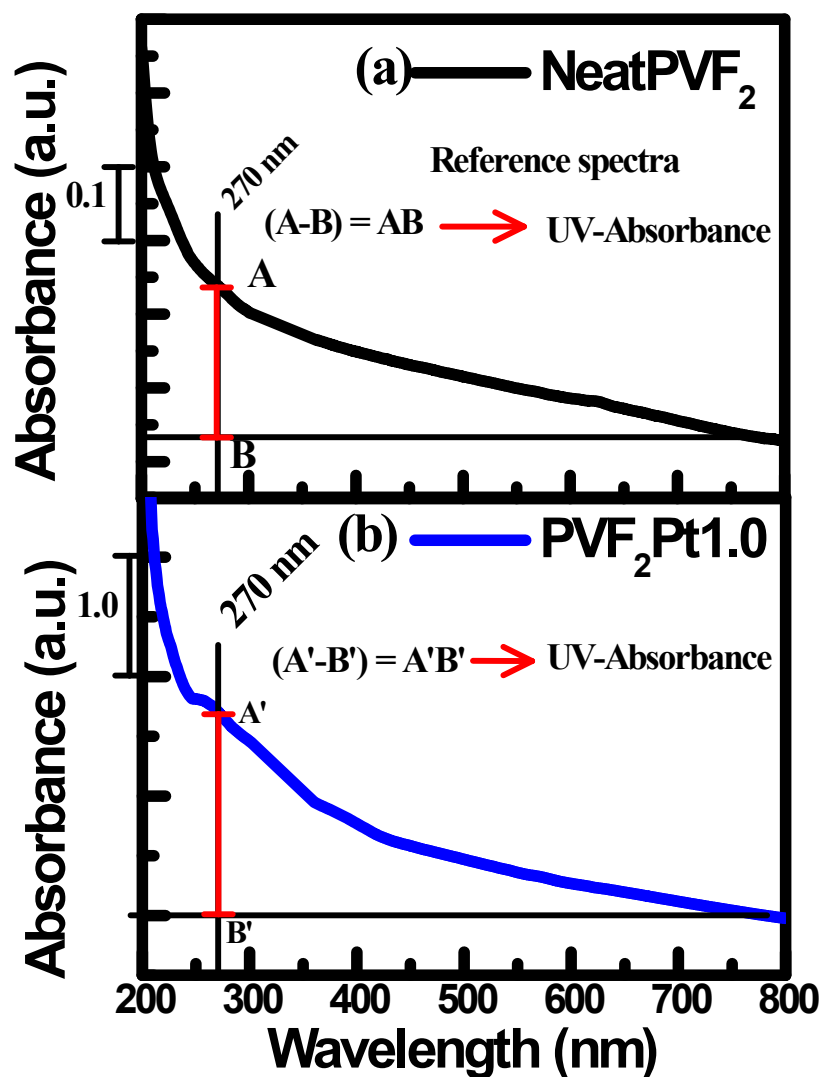


Figure S2. The degree of UV-Absorbance estimated from UV-Vis spectra where the absorbance at 270 nm (*i.e.*, AB shown in (a)) from NeatPVF₂ is taken as reference absorbance. Likewise, the absorbance at 270 nm from Pt-NPs doped PVDF films (for example, A'/B' in PVF₂Pt1.0 film, shown in (b)) is considered.

The degree of UV-Absorption at 270 nm is calculated from UV-Vis spectra of Pt-NPs doped PVDF films considering NeatPVF₂ film as a reference as shown in Figure S2 (a~b) with the following equation.

$$\text{Degree of UV - Absorption} = |A'B' - AB| \times |t_f| \times 100\%$$

Where, $|t_f|$ is the thickness factor.

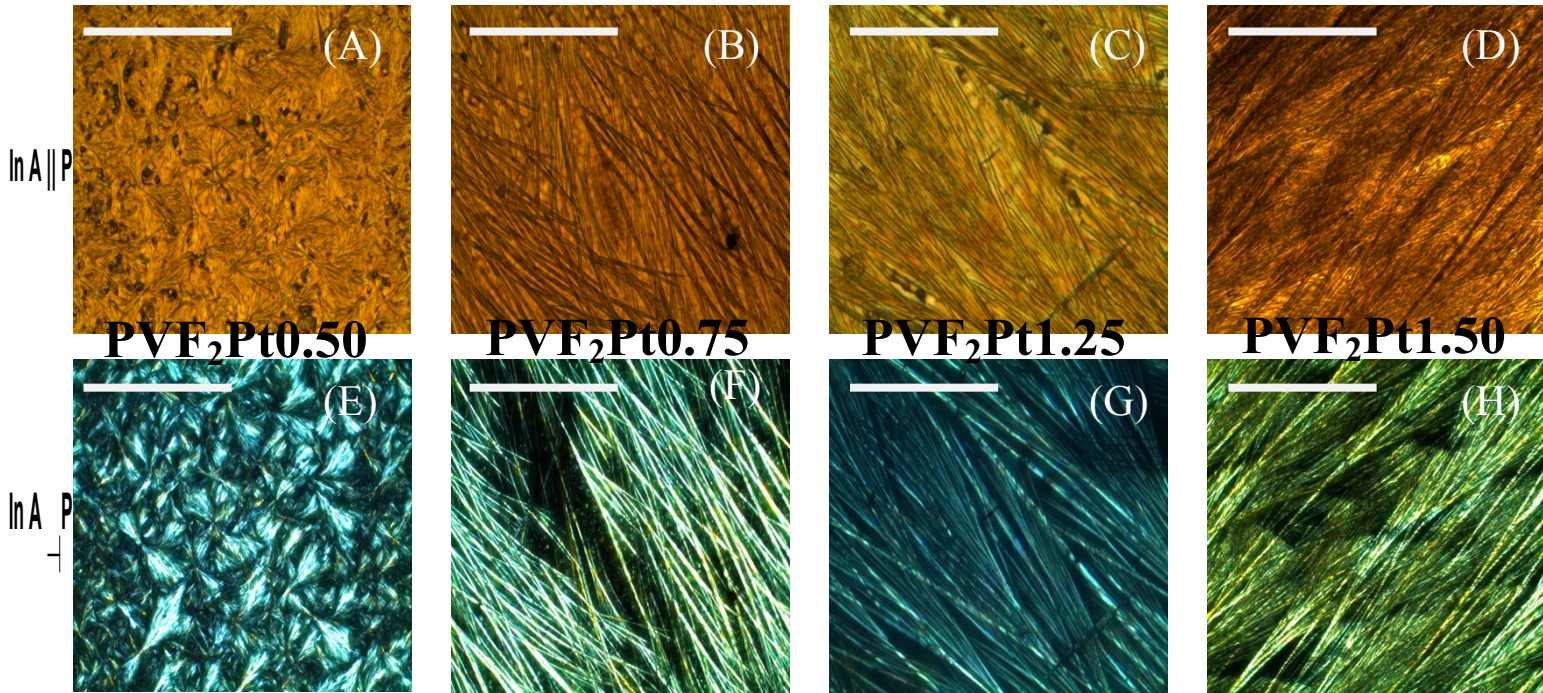


Figure S3. Optical microscopic images of PVF₂Pt0.50, PVF₂Pt0.75, PVF₂Pt1.25, PVF₂Pt1.50 films both in unpolarize (A||P) [A~D] and polarize (A⊥P) [E~H] modes. The scale bars given on the images are representing 100 μm in length.

The optical microscopic images of Pt-NPs doped PVDF films (PVF₂Pt0.50, PVF₂Pt0.75, PVF₂Pt1.25 and PVF₂Pt1.50) are shown in Figure S3. The morphology of these Pt-NPs doped PVDF films are in unpolarize mode (A||P) (Figure S3 (A~D)). The increasing tendency of fibril growths over the PVDF surface are observed with increasing concentration of Pt-salt. In cross polarize mode (A⊥P) (shown in Figure S3, E~H) the intense birefringent fibrils are visible and it obscures the typical small γ spherulitic structure in the surface of the film.

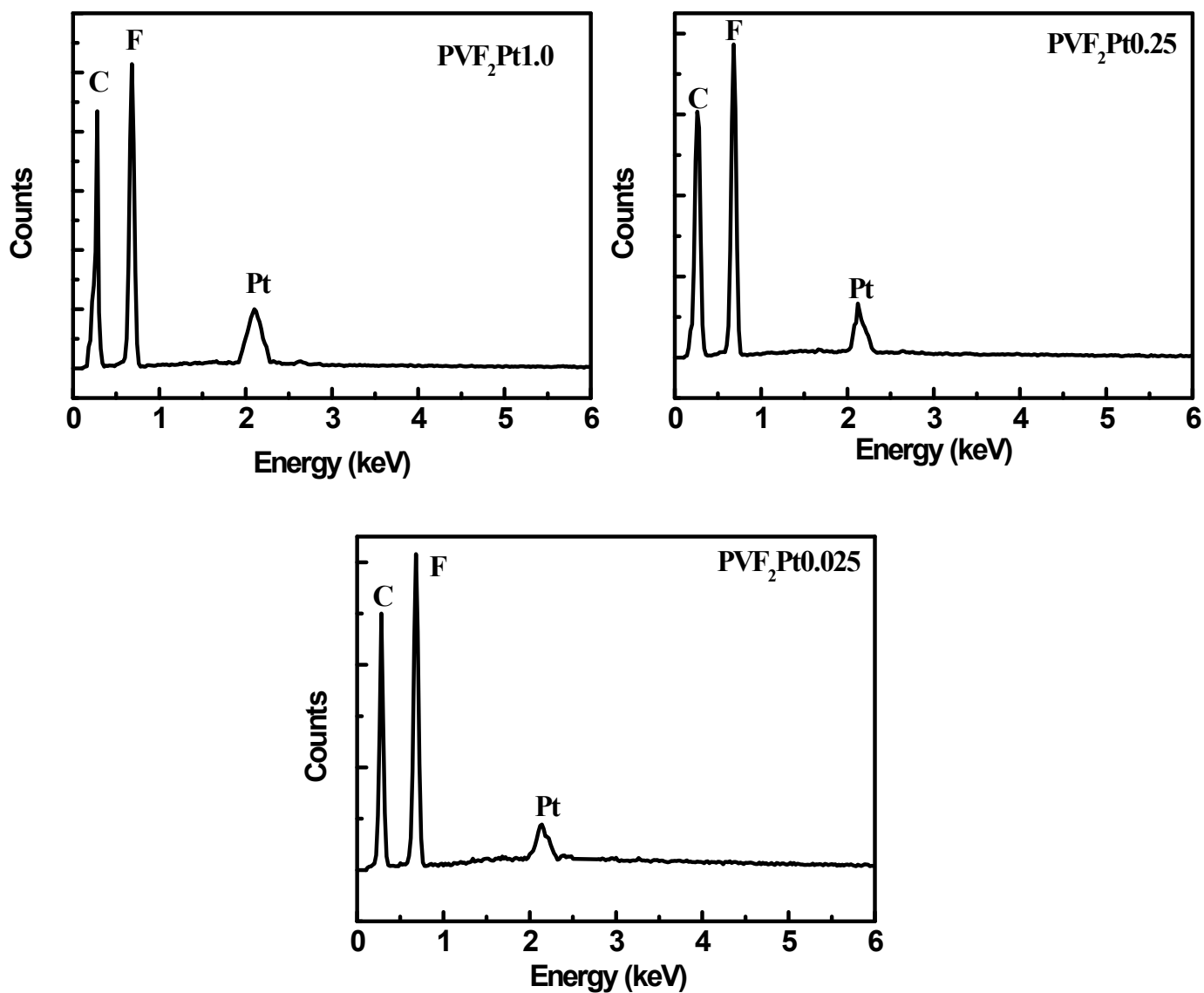


Figure S4 EDS spectrum of Pt-NPs doped PVDF films. It exhibits almost equal (1:1) carbon(C) and fluoride (F) signal arising from PVDF and a prominent peak from elemental Pt.

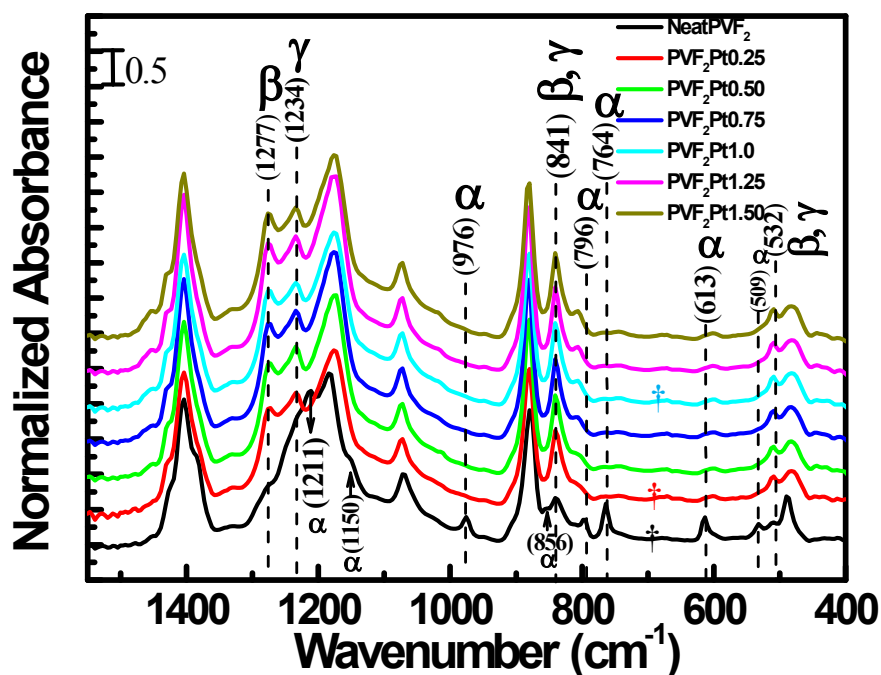


Figure S5. FT-IR spectra (1550 – 400 cm^{-1} frequency region) of Pt-NPs added PVDF films. The † marked (with suitable colour code) samples are represented in the main article.

The FT-IR spectra of Pt-NPs doped PVDF films show a subsequent increase of 841 cm^{-1} band with increasing amount of Pt-salt beyond 1.0 wt% , no further significant improvement is noticed. That means, in PVF₂Pt1.0 film complete nucleation of electroactive phases has taken place.

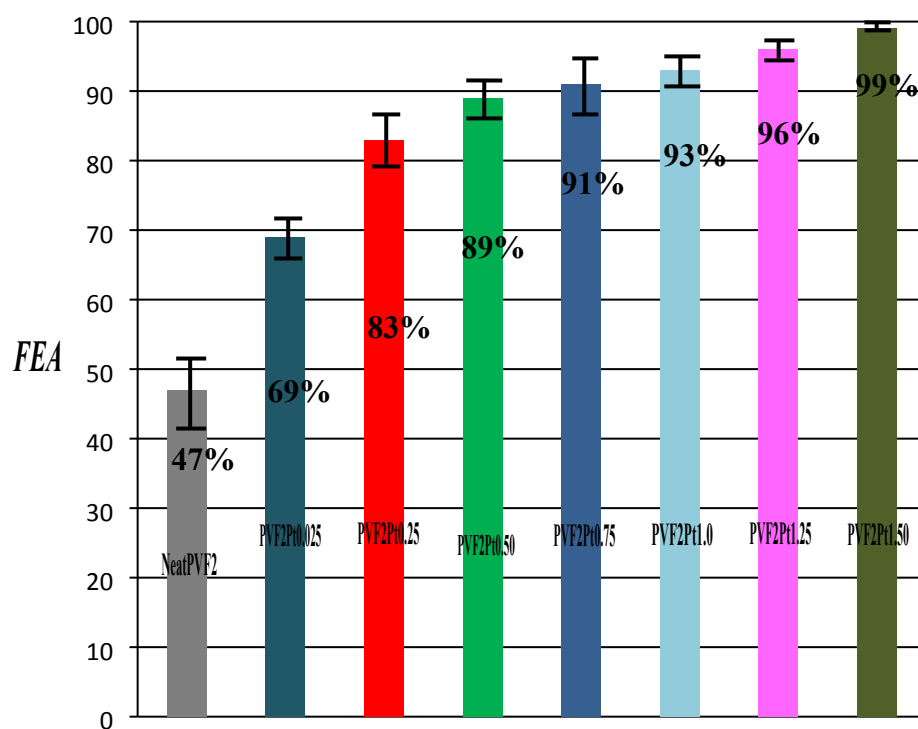


Figure S6. The percentage (%) of F_{EA} for NeatPVF₂ and Pt-NPs doped PVDF films

It is clearly observed that maximum of 99 % of electroactive phase can be achieved by 1.5 wt% of Pt-NPs doping in PVDF matrix. After 1.0 wt% of Pt-salt loading in PVDF, the percentage increase of F_{EA} in Pt-NPs doped PVDF films is not as steep as observed below that wt% of Pt-NPs loading in PVDF matrix.

Table S7

| Name of the Samples | $\frac{\sum A_{cr}}{\sum A_{amr}}$ | $\chi_c = \frac{\sum A_{cr}}{\sum A_{cr} + \sum A_{amr}} \times 100\%$ |
|--------------------------|------------------------------------|------------------------------------------------------------------------|
| NeatPVF ₂ | 1.0 | 50% |
| PVF ₂ Pt0.025 | 0.76 | 43% |
| PVF ₂ Pt0.25 | 0.64 | 39% |
| PVF ₂ Pt1.0 | 0.52 | 34% |

Table S8

| Sample Name | $\chi_\beta(\%) = F(\beta) \times \chi_c(\%)$ | $\chi_\gamma(\%) = F(\gamma) \times \chi_c(\%)$ |
|--------------------------|-----------------------------------------------|-------------------------------------------------|
| PVF ₂ Pt0.025 | 21 % | 9 % |
| PVF ₂ Pt0.25 | 28 % | 4 % |
| PVF ₂ Pt1.0 | 30 % | 2 % |

Footnote: Here $F(\beta)$ and $F(\gamma)$ is obtained from Figure 8 of main article.

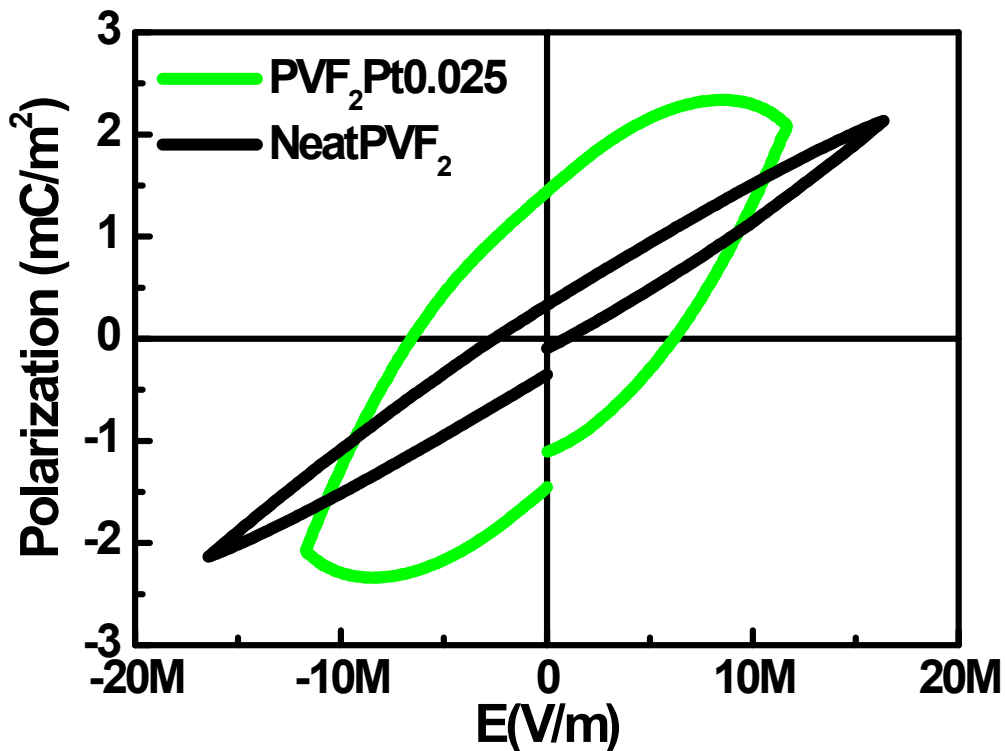


Figure S9. P-E loops of NeatPVF₂ and PVF₂Pt0.025 films.

Figure S9 compares the polarization-electric field (P - E) loops of the NeatPVF₂ and PVF₂Pt0.025 films. Ferroelectric P - E loops characterized with hysteresis, remnant polarization (P_r) and coercive field (E_c) have been observed in the films. A more pronounced improvement (five times) of P_r value in Pt-NPs doped PVDF film (PVF₂Pt0.025) compared to the NeatPVF₂ originates due to the presence of polar β - and γ - phases. Furthermore, it can be improved by controlling the film preparation parameters where the orientation of the molecular dipoles can be monitored⁴ (main article). In addition the coercive field improved (six times) in Pt-NPs doped PVDF film (PVF₂Pt0.025) than the NeatPVF₂ is well correlated with the enhancement of crystallite size and chain orientation. Since the piezoelectric coefficient is

directly proportional to the remnant polarization in the PVDF based ferroelectric polymers, higher P_r and E_c are anticipated in $PVF_2Pt0.25$ and $PVF_2Pt1.0$ films.

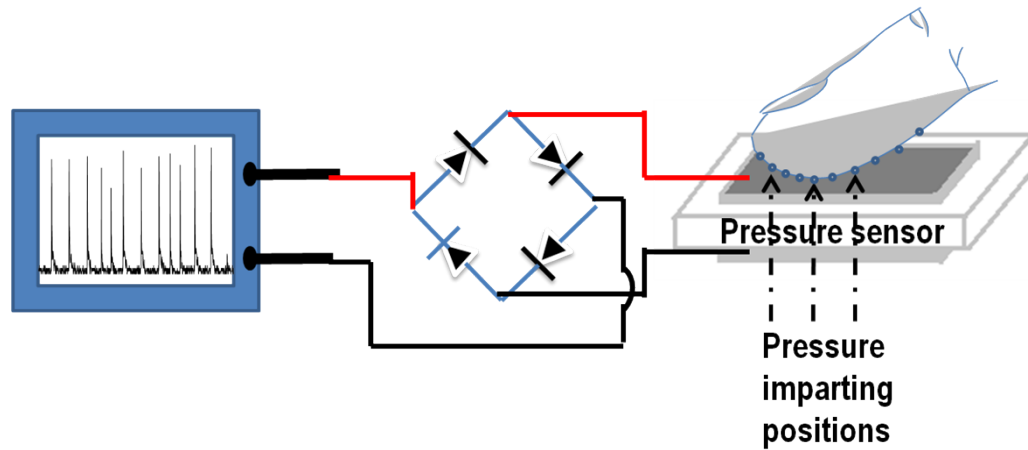


Figure S10. Schematic circuit diagram with full wave bridge rectifier for detecting the human finger touch signal (in terms of voltage) from tactile sensor made with PVDF films.

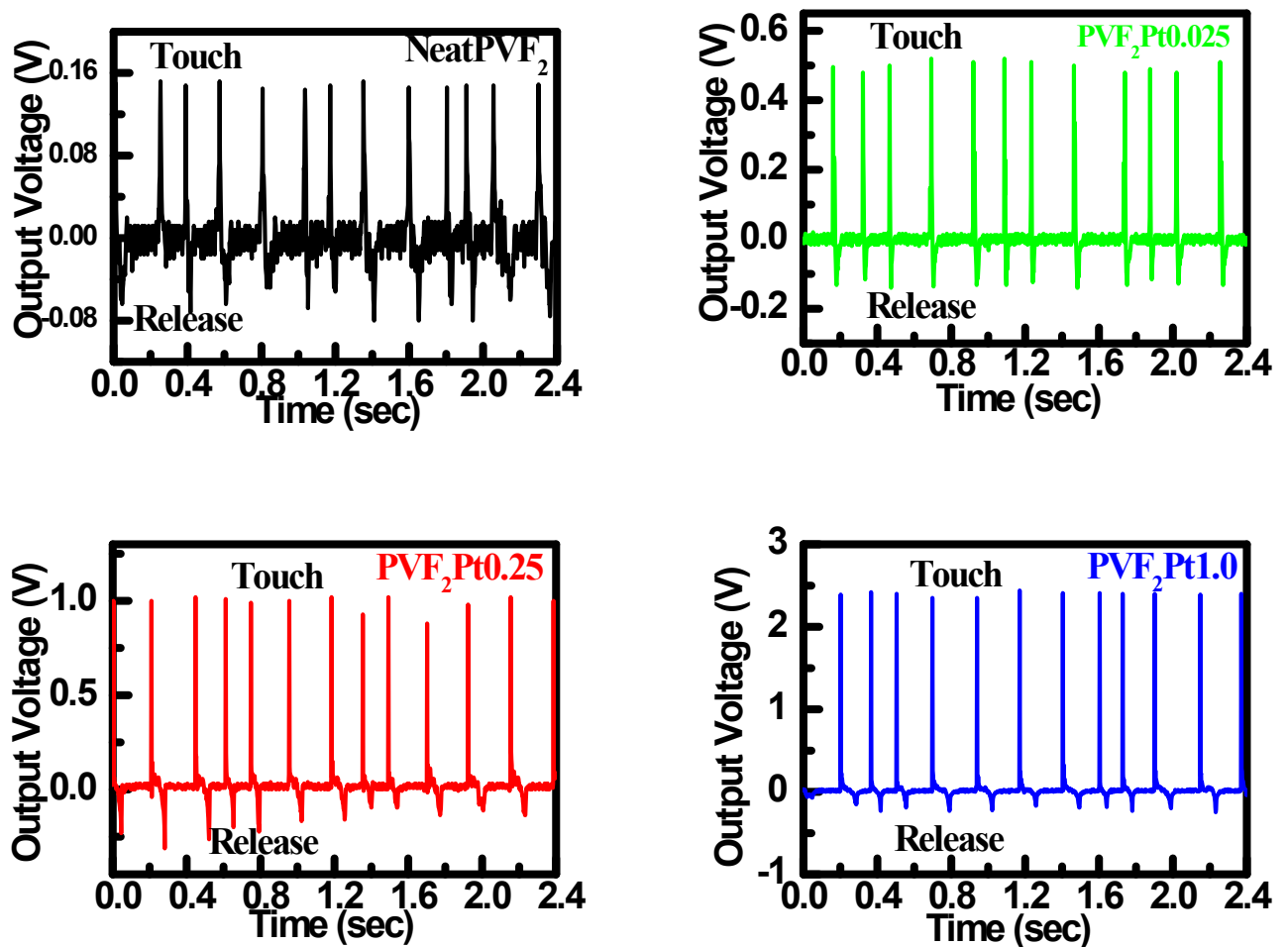


Figure S11. The human finger touch responses from tactile sensors made from of Neat PVDF as well as Pt-NPs doped PVDF films are shown.

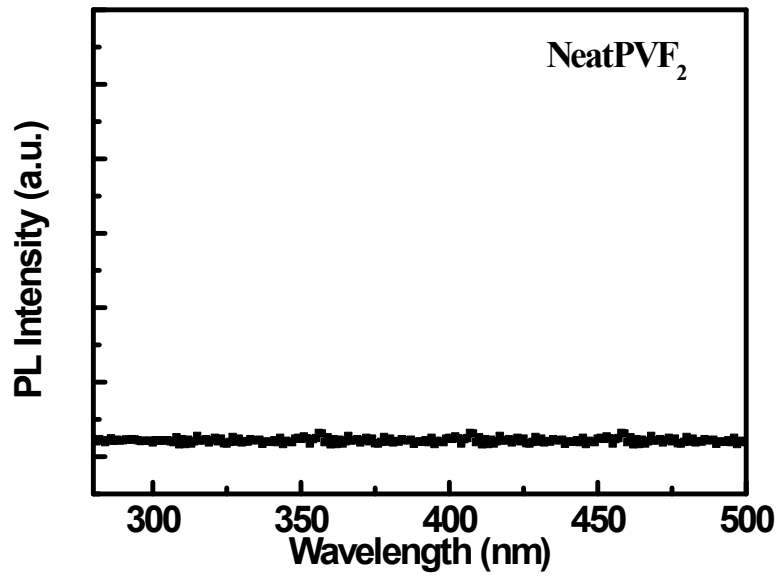


Figure S12. The PL-signal from NeatPVF₂ film, which gives no luminescence under the excitation of 260 nm.

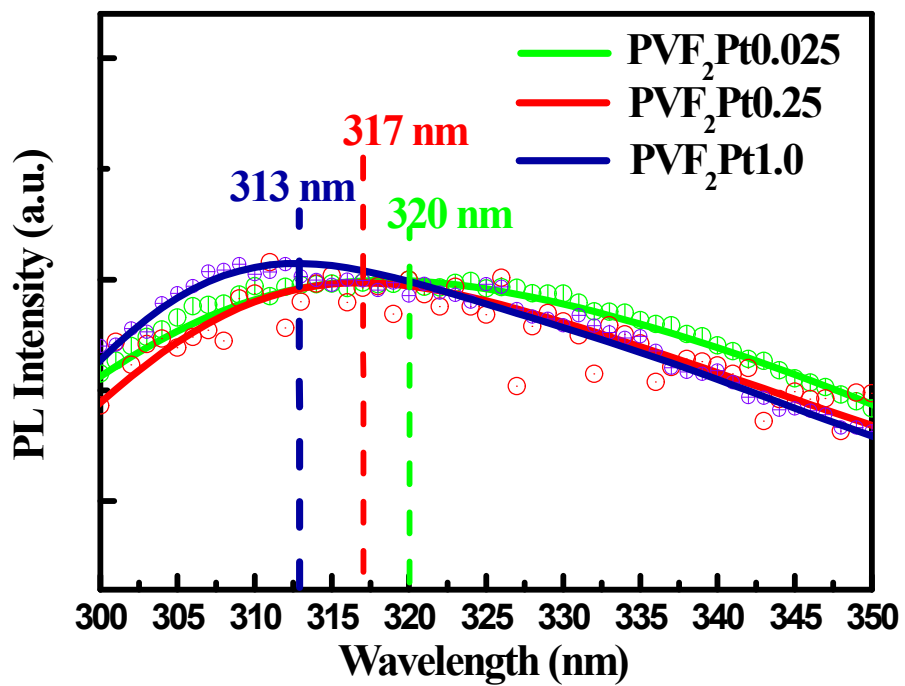


Figure S13. The blue shifts of PL-spectrum with increasing amount of Pt-NPs in doped PVDF films are shown.