



# Investigating the electronic properties of PANI/graphene/PVDF/PTFE nanocomposite

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Received: 15 October 2023 / Accepted: 7 January 2024 / Published online: 12 February 2024  
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## Abstract

Manufacturing of clean energy is an important topic of research for modern life. This paves the way toward investigating easy manufacturing; high-performance energy storage materials. In this sense, conducting polymers such as polyaniline (PANI) are modified with graphene (G) then bound with poly vinylidene fluoride (PVDF) and poly tetrafluoro ethylene (PTFE) to enhance their electronic properties to be used as electrode material in energy storage applications. Furthermore, molecular modeling based on density functional theory at B3LYP/LanL2DZ level of theory was utilized to study the interaction between PANI; G; PVDF and PTFE. Some important properties are calculated such as the total dipole moment (TDM), HOMO/LUMO energy gap ( $\Delta E$ ), and molecular electrostatic potential (MESP). TDM of PANI was found to be 3.994 Debye and increased to 6.010, 9.012, and 9.822 Debye for PANI/G/PTFE, PANI/G/PVDF/PTFE, and PANI/G/PVDF, respectively.  $\Delta E$  of PANI is 4.353 eV and decreased because of the interaction of PANI with G and polymer binders to reach 3.507, 3.095, and 2.127 eV for PANI/G/PTFE, PANI/G/PVDF, and PANI/G/PVDF/PTFE, respectively. From MESP result, the reactivity and electronic properties increased with the interaction of PANI with G and polymer binders. PANI/G/PVDF/PTFE composite was dedicated as the most suitable candidate for electrode material for many applications.

**Keywords** Conducting polymers · B3LYP · LanL2DZ · TDM · HOMO · LUMO · MESP

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## 1 Introduction

Smart technology and flexible electronics are important to our life and have become a part of energy storage devices that are eco-friendly and cost-effective like supercapacitors (Arthisree and Madhuri. 2020; Pal et al. 2021; Liu et al. 2021). Supercapacitors are higher in energy density than ordinary capacitors and have fast charge and discharge rates, high power density, and a long-life cycle. Because of these desirable properties, are used in applications like medical devices and electric vehicles (Pal et al. 2020; Li et al. 2021; Kung et al. 2021). Electrode materials play an important role in energy storage devices such as supercapacitors. Therefore, improving electrode material is important for enhancing the supercapacitors' performance (Wang et al. 2016; Ghanem et al. 2023). The usual choices of materials used as electrodes for energy storage devices as supercapacitors are conducting polymers and carbon-based materials, transition metal oxides, and their possible composites (Wang et al. 2016; Rego et al. 2023).

Conducting polymers have interesting characteristics, and so they are suitable for potential applications like sensors, thermoelectric devices, solar energy, corrosion resistance applications, photocatalysts, and energy storage device such as supercapacitor (Almasi et al. 2016; Ashokkumar et al 2020). Conducting polymers like polythiophene, polypyrrole (Ppy), polyaniline (PANI), and their derivatives are conducting in nature as they have extended  $\pi$ -conjugation (Salehi et al. 2022; Wang et al. 2016; Verma et al. 2022).

PANI is one of the conducting polymers and is the most used by researchers. PANI has a unique structure and is suitable for electrode material for many applications, such as supercapacitors, because of its low cost, high-power density, high flexibility, high specific capacitance, easy preparation, with the presence of functional groups with environmental stability. PANI can be found in different oxidation states, namely leucoemeraldine (fully reduced), pernigraniline (fully oxidized), and half-oxidized emeraldine base, which, after protonation, is the most stable conductive state but leucoemeraldine and pernigraniline are still insulators after protonation. For applications such as electrode materials, PANI is used as a mixture of both oxidation states, with the exception of the best performance in the mixture being the high emeraldine base portion (Mazlan et al. 2019). It is reported that 1% toluene-4-sulfonic acid monohydrate -doped PANI film was fabricated with concentrations up to 6 wt% of N-methyl-2-pyrrolidone as a solvent. Results indicated that the specific electrical conductivity did not significantly change with changing concentrations. Doped PANI at a concentration of 3% is dedicated to both sensing and supercapacitor applications (Wang et al. 2016). Furthermore, an overview was conducted for both polyaniline and polyaniline thin films, indicating different preparations and characterizations in order to assign suitable applications based on their investigated properties (Beygisangchin et al. 2021b). The effect of toluene-4-sulfonic acid monohydrate with different concentrations on the properties of PANI was studied. It is found that, photoluminescence spectroscopy indicating that, the PANI is a good candidate for Pyrene detection (Beygisangchin et al. 2022). The same spectroscopic tool was also utilized for possible application of PANI for Fluorene detection (Beygisangchin et al. 2021a).

Graphene (G) is a material consisting of carbon atoms having  $SP^2$  hybridization arranged in a two-dimensional honeycomb lattice nanostructure. It has some unique properties, such as high surface area, many active sites, high electrical conductivity,

good specific capacitance, and high ion–electron transport, and is therefore widely used in energy applications such as supercapacitors (Bo et al. 2023).

Carbon-based electrode materials like G could be applied as supercapacitor with high power density and high cycling stability, but they have a low energy density, which limits their mechanism of energy storage (Wang et al. 2016). PANI as an active material in supercapacitors does undergo a redox reaction as it has different oxidation states, and through the pseudo-capacitive processes, the polymer cracking through doping and de-doping of charged ions is causing low cycle stability, and PANI may be degraded at high potentials because of over-oxidation. Therefore, PANI electrodes work at low potentials, and because of this limitation, PANI is needed to form composites with other materials to develop PANI electrodes (Wang et al. 2016).

Consequently, to enhance the low cycle stability during the charge–discharge processes of PANI electrodes, PANI is combined with metal oxide and carbonaceous materials like G-forming polymer-based composites that improve the conductivity and cycle stability of the electrode as when graphene's interaction with polymer enhances the recyclability, improves the mechanical strength, and increases the surface area of the supercapacitor (Baby et al. 2023; Salehi et al. 2022; Wang et al. 2016; Verma et al. 2022; Usman et al. 2019; Kenesi et al. 2022; Majeed et al. 2022; Gaikwad et al. 2023; Varghese et al. 2023).

Composite materials are formed by combining different materials to obtain their best properties. Polymer composites are desirable because of their thermal and mechanical properties, which make them suitable for many applications such as energy storage, electronics, and surface coatings (Saikia et al. 2020). Therefore, the combination of conducting polymers with carbon materials and metal oxides enhances performance by obtaining the advantages of each component (Wang et al. 2016).

Polymer binders improve the electrode material in supercapacitors as the binders are used as a glue that holds components of energy storage devices together. The binder is electrochemically inert but has the strength to introduce mechanical support and help disperse components during the fabrication process in the solvent. They also increase the performance and flexibility of the electrode in supercapacitors as they provide mechanical support, especially for hybrid supercapacitors that include faradaic redox reaction, which cause physical damage to the structure of the electrode and a change in the volume of the electrode. The presence of a binder helps the active material in faradaic redox reactions as the binder suppresses the change in volume of the active material, while its chemical inertness in the supercapacitor protects the electrode from corrosion (Salleh et al. 2023; Cholewinski et al. 2021).

Different binders were used to prepare electrode materials in supercapacitors, such as poly vinylidene fluoride (PVDF), poly tetrafluoro ethylene (PTFE), and Nafion (Salleh et al. 2023). Fluoropolymers like PVDF and PTFE are used as polymer binders that decrease G agglomeration and improve the mechanical strength and stability of electrode (Varghese et al. 2023).

PVDF and PTFE are electroactive polymers which can change their shape and size in response to electric stimulation, and they are used as separators, electrolytes, and binders in manufactured supercapacitors. PVDF has various properties, such as high impact resistance, light weight, piezoelectric property, high dielectric constant, and mechanical and electrochemical stability. As a binder, it also has high thermal and mechanical stability and non-reactivity. The strong adhesive property of PVDF holds the active material of the working electrodes together and causes an increase in the specific capacitance. The

modification of G by PVDF shows good conductivity, and thermoplastic properties, ductility. (Rajeevan et al. 2021).

Another important application of functionalized PANi was reported.

Box-Behnken design was used to optimize the physical factors of Chitin-grafted PANI for  $\text{NH}_3$  gas sensor detection (Sambasevam et al. 2023). Another functionalization of PANI was also tried with chitin in order to optimize its use to remediate Cr from wastewater. It was dedicated as an eco-friendly active surface for the removal of Cr (Shahabuddin. et al. 2022).

Rather than experimental efforts, computational methods show potential use for investigating the electronic properties of many systems. Molecular modeling with various levels of theory is used for the investigation of the electronic, chemical, and physical properties of many systems, such as nanomaterials. Synthetic and natural polymers could be studied by molecular modeling, and some important parameters could be calculated, such as total dipole moment (TDM), HOMO/LUMO energy gap ( $\Delta E$ ), and molecular electrostatic potential (MESP), and these physical properties reflecting the reactivity of the studied structure (Badry et al. 2020b).

The present work is conducted to study the electronic properties of PANI/G/PVDF/PTFE nanocomposite using density functional theory (DFT). So, the interaction between PANI and G and polymer binders like PVDF and PTFE was studied. Some important properties are calculated, such as TDM,  $\Delta E$ , and MESP, to elucidate certain applications based on the calculated electronic properties. The overall aim is to enhance the electronic properties of PANI electrodes by adding G and polymer binders to it.

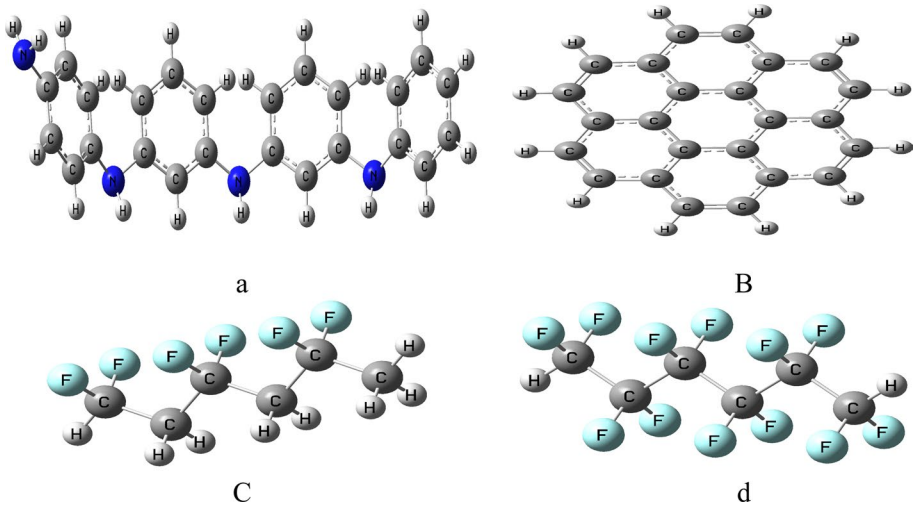
## 2 Calculation details

All the studied model molecules were subjected to quantum mechanical calculations utilizing the DFT. Calculations were implemented with Gaussian 09 soft code (Frisch et al. 2010) that utilizes a basis set of Gaussian-type orbital functions. The Becke -three parameters -Lee Yang-Parr hybrid functional (B3LYP) (Becke. 1993; Lee et al. 1988; Miehlich et al. 1989) with basis set LanL2DZ is employed in the calculations at Molecular Modeling and Spectroscopy Laboratory, Centre of Excellence for Advanced Science, National Research Centre, Egypt. The effect of polymer binder on the physical properties of PANI and PANI/G composite was studied. TDM,  $\Delta E$ , and MESP were calculated for the studied structures at the same level of theory.

## 3 Results and discussion

### 3.1 Building model molecules

The first step before the attachment of the polymer binder to the PANI/G composite is describing how the model molecules were built. In Fig. 1, a sheet of G consisting of 24 carbon atoms, four units of PANI, three units of PVDF, and three units of PTEF are chosen for model molecules, and Fig. 2 demonstrates the interaction between them, showing the composites formed with PANI and G. The interaction of PANI, and PVDF or PTFE and G occurred from the amine group of PANI based on the previous finding (Badry et al. 2020b).



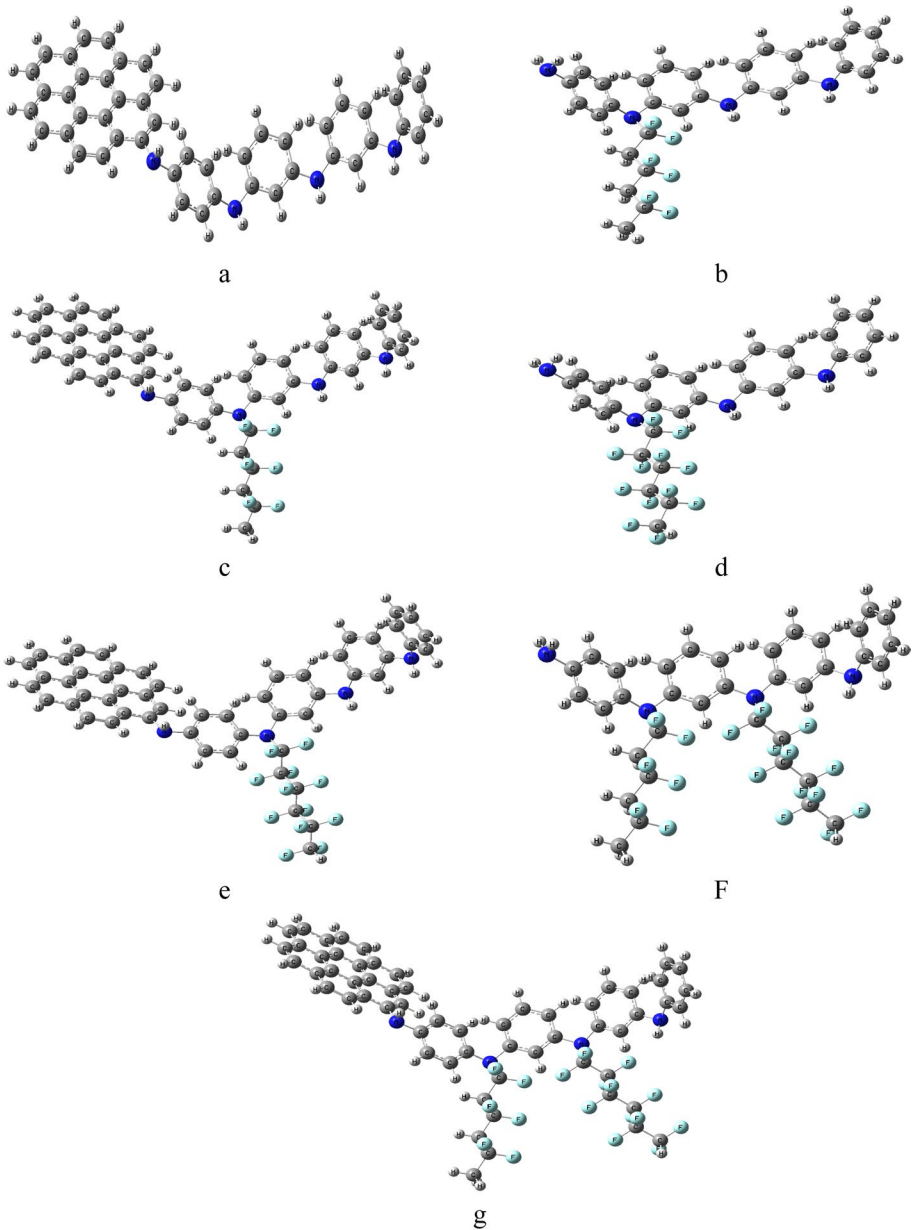
**Fig. 1** Optimized structures of **a**-PANI, **b**- G, **c**- PVDF and **d**- PTFE

In Fig. 2a, the G sheet could interact with PANI through the first amine group, and in Figs. 2b and 2d, the PVDF and PTFE could interact with PANI through the second amine group, respectively. As shown in Fig. 2c, the G sheet could interact with PANI through the first amine group, and PVDF could interact with PANI through the second amine group. As demonstrated in Fig. 2e, the G sheet could interact with PANI through the first amine group, and the PTFE could interact with PANI through the second amine group, while in Fig. 2f, the PVDF could interact with PANI through the second amine group and the PTFE could interact with PANI through the third amine group. In Fig. 2g, the G sheet could interact with PANI through the first amine group, PVDF could interact through the second amine group, and PTFE could interact through the third amine group, such that the interaction of PVDF was proposed to take place through an H atom of PVDF, and the same for PTFE and G.

### 3.2 Electronic properties

In order to study the electronic properties of the interaction of PANI with G to form composites, and with PVDF and PTFE as polymer binders, TDM and  $\Delta E$  are calculated. TDM can be defined as the initial derivative of energy with respect to an electric field. It is thought to be an indicator of an asymmetry in the charge distribution. It is said that a large dipole moment for a specific structure indicates its capacity to quickly interact with the surrounding molecules. It was reported that an increase in TDM values associated with a decrease in  $\Delta E$  values could be descriptors for reactivity when correlated with  $\Delta E$  values. TDM measures the reactivity of material in Debye, while  $\Delta E$  can refer to the electronic form of the material (EIDesouky et al. 2021).

Table 1 represents the changes in TDM and  $\Delta E$  of PANI, G, PVDF, PTFE and their interaction. The TDM of PANI, G, PVDF, PTFE is 3.994, 0.000, 8.403, 0.000 Debye, respectively, and  $\Delta E$  of PANI, G, PVDF, PTFE is 4.353, 4.026, 10.457, 8.791 eV, respectively.



**Fig. 2** Optimized structures of **a-** PANI/G, **b-** PANI/PVDF, **c-** PANI/G/PVDF, **d-**PANI/PTFE, **e-**PANI/G/PTFE, **f-** PANI/PVDF/PTFE and **g-** PANI/G/PVDF/PTFE

The TDM of PANI changed because of the interaction with G to be 3.039 Debye for PANI/G composite. The TDM of PANI increased from 3.994 Debye to 6.010, 6.977, 9.012,

**Table 1**  $\Delta E$  as eV and TDM as Debye of PANI/G and polymer binder calculated at DFT: B3LYP/LanL2DZ

Structure	TDM	$\Delta E$
PANI	3.994	4.353
G	0.000	4.026
PVDF	8.403	10.457
PTFE	0.000	8.791
PANI/G	3.039	3.236
PANI/PVDF	10.569	4.130
PANI/PTFE	6.977	4.092
PANI/PVDF/PTFE	11.229	3.979
PANI/G/PVDF	9.822	3.095
PANI/G/PTFE	6.010	3.507
PANI/G/PVDF/PTFE	9.012	2.127

9.822, 10.569, and 11.229 Debye for the PANI/G/PTFE, PANI/PTFE, PANI/G/PVDF/PTFE, PANI/G/PVDF, PANI/PVDF, and PANI/PVDF/PTFE, respectively.

On the other hand,  $\Delta E$  decreased from 4.353 eV for PANI to 4.130, 4.092, 3.979, 3.507, 3.236, 3.095, and 2.127 eV for PANI/PVDF, PANI/PTFE, PANI/PVDF/PTFE, PANI/G/PTFE, PANI/G, PANI/G/PVDF, and PANI/G/PVDF/PTFE, respectively.

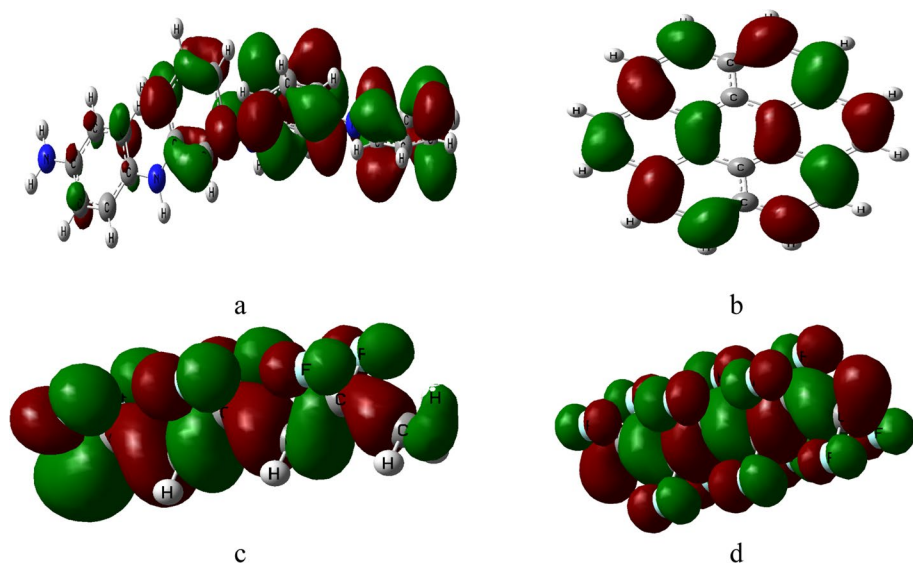
The interaction of PANI/G composite with PVDF and PTFE individually, and with both of them together forming PANI/G/PVDF, PANI/G/PTFE, PANI/G/PVDF/PTFE composites resulted in increase in TDM and decrease in  $\Delta E$  of PANI, indicating that the interaction of PANI with G, PVDF and PTFE is a strong interaction and increases the reactivity, and enhanced the electronic properties of PANI and PANI/G composite with the PANI/G/PVDF/PTFE composite having the lowest  $\Delta E$  of 2.127 eV, and that increases the conductivity and the specific capacitance compared to PANI and PANI/G composite, thus enhancing the cyclic stability of electrode as previously report that the decrease in  $\Delta E$  showed improvement in the specific capacitance and reflected to electrode measurement as enhanced cyclic stability and lower  $\Delta E$  showed higher electrical conductivity (Almasi et al. 2016; Ashokkumar et al. 2020).

Figures 3 and 4 represent the HOMO/LUMO molecular orbitals for PANI, G, PVDF, PTFE and show the interaction of PANI with G, and their interactions with the polymer binders PVDF and PTFE to form composites. Values of  $\Delta E$  and TDM resulting from the proposed interactions are presented in Table 1.

### 3.3 Molecular electrostatic potential

The MESP contour maps are a physical description of the surface of each investigated structure. Studying MESP is considered a useful tool for describing the distribution of electronic charges. Practically, this could be an indicator for studying the active sites that found in the proposed chemical structure.

The MESP is indicated in terms of so-called color map. This mapping is shown by a contour that uses colors to describe the charge distributions for the examined structure, the electronegativity is represented by the color scheme red > orange > yellow > green > blue, which describes the electron distribution. The red color represents the most electronegative regions which indicate the active sites, and the yellow color represents the neutral regions



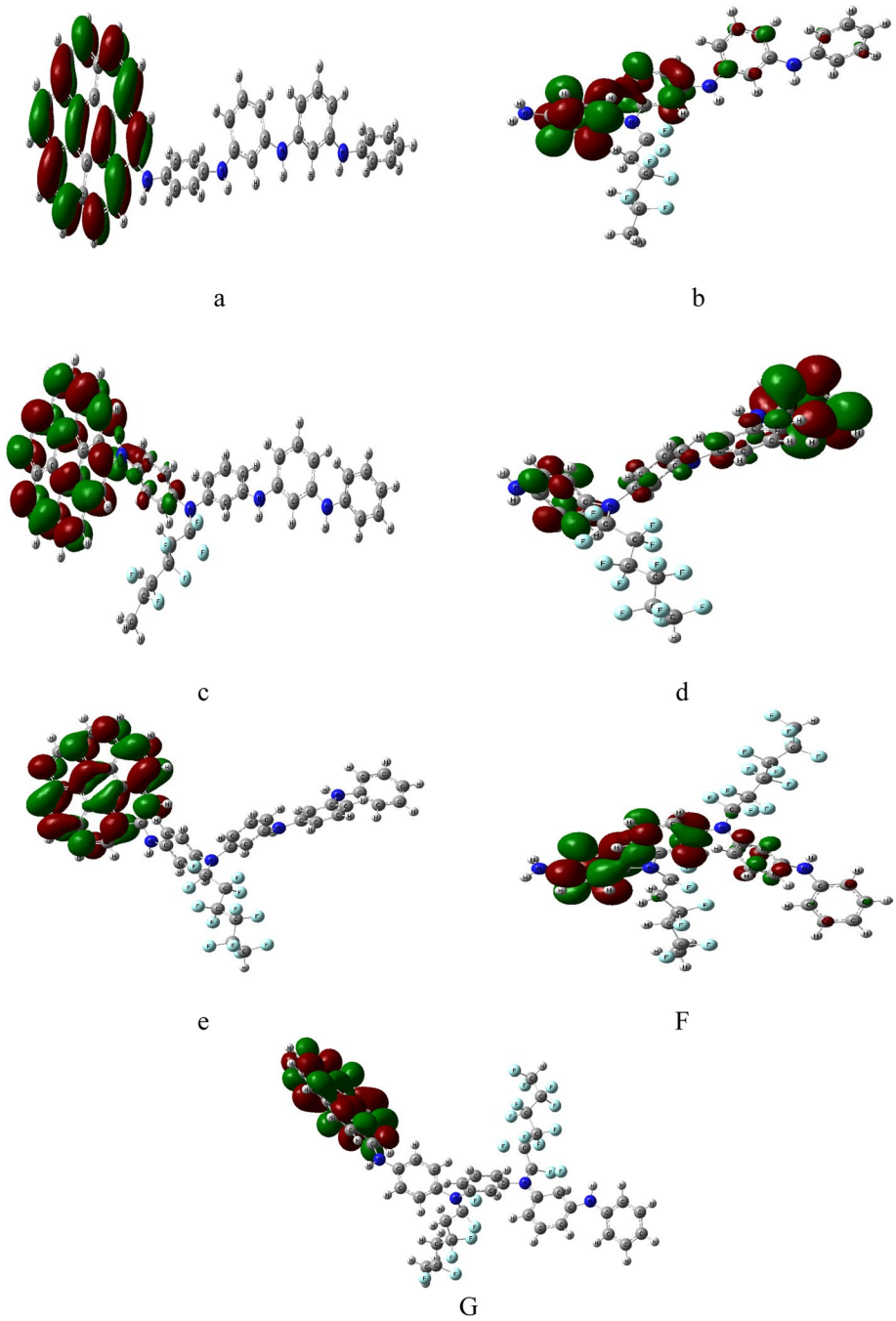
**Fig. 3** B3LYP/LanL2DZ calculated HOMO/LUMO molecular orbitals for **a**-PANI, **b**-G, **c**-PVDF and **d**-PTFE

while the most positive regions are represented by blue color (Sobhy et al. 2023; Omar et al. 2023; Badry et al. 2020a and b).

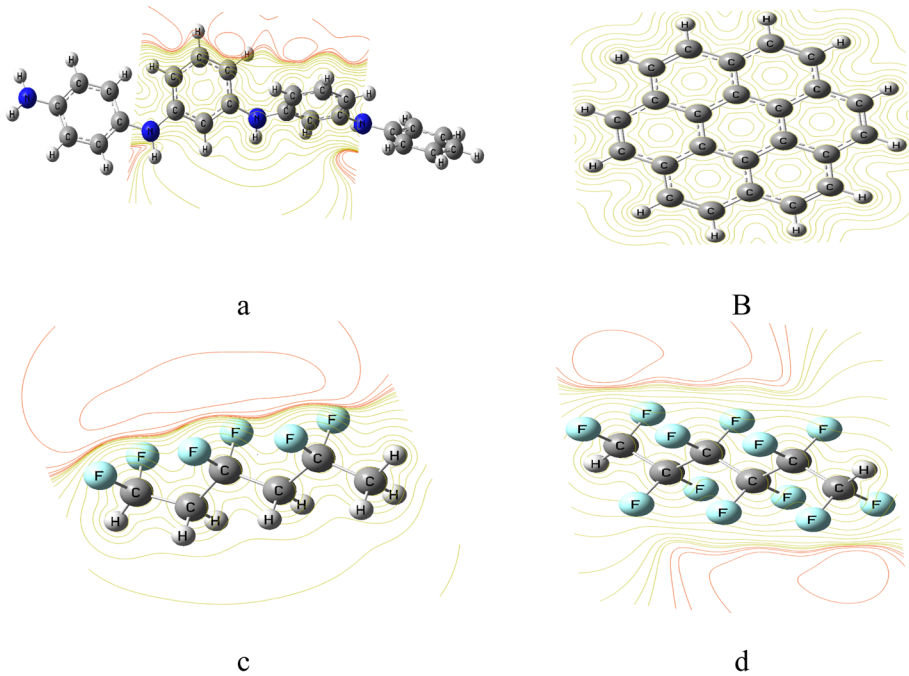
Figure 5 represents the MESP maps calculated for PANI, G, PVDF and PTFE. This figure shows that the intensity of red color around the surface of PANI indicates that the electronic charges are distributed on its surface as increased electronegativity indicated by the increased density of the red color (Sobhy et al. 2023) while the intensity of yellow color around the surface of G indicates its neutral surface. For PVDF, the negative charges are distributed around its active site of the F atoms, and similarly in PTFE the negative charges are distributed around its surface from its active site of the F atoms, such that the increase in the density of red color reflects their increased electronegativity.

Figure 6 represents the MESP map calculated for the interaction of PANI with G, PANI with PVDF, PANI/G composite with PVDF, PANI with PTFE, PANI/G composite with PTFE, PANI with PVDF and PTFE, and PANI/G with both PVDF and PTFE altogether. The figures show redistribution of the charges on PANI/G composite and an increase in the density of red color at the site of G interaction with PANI, indicating redistribution of the electronic charges and reflecting more electronegativity, such that the most active site on PANI is from the site of interaction with G. The interaction of PVDF with PANI increased the reactivity around the surface of PANI and around the F atoms, the active site of PVDF in PANI/PVDF, representing an increase in the density of red color at these sites.

In the case of PANI/G/PVDF composite, the reactivity is increased with the redistribution of the electronic charges more than PANI/G composite and showed increase of electronic charges around G site and F atoms on PVDF site more than that in PANI/G composite. The addition of PTFE to PANI increased the reactivity of PANI as the interaction with PTFE increased the electronic charges around the surface of PANI/PTEF



**Fig. 4** B3LYP/LanL2DZ calculated HOMO/LUMO molecular orbitals for **a**-PANI/G, **b**- PANI/PVDF, **c**- PANI/G/PVDF, **d**-PANI/PTFE, **e**-PANI/G/PTFE, **f**- PANI/PVDF/PTFE and **g**- PANI/G/PVDF/PTFE



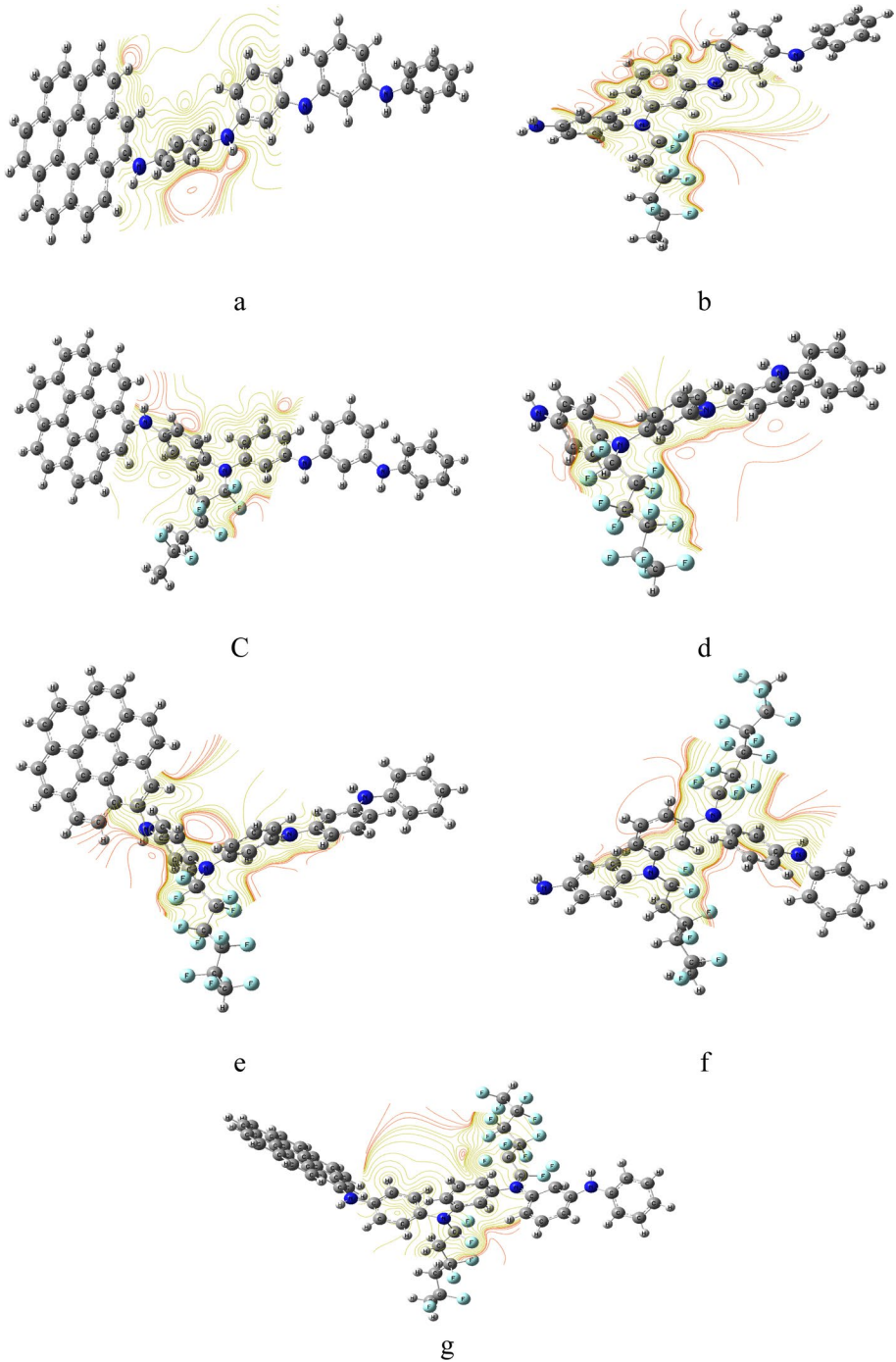
**Fig. 5** B3LYP/LanL2DZ calculated MESP for **a-** PANI, **b-** G, **c-** PVDF and **d-** PTFE

more than PANI/PVDF as PANI/PTEF has higher density of red color than PANI/PVDF, indicating its more electronegativity.

In the case of PANI/G/PTFE composite, there was an increase in the distribution of electronic charges on it around PANI's surface and G site and around the PTEF surface, which increased the reactivity of PANI/G/PTFE composite more than PANI/G/PVDF composite as PANI/G/PTFE has a higher density of the red color than PANI/G/PVDF, indicating its higher electronegativity.

For the PANI/PVDF/PTFE composite, the electronic charge distribution around its surface showed an increase in the density of the red color around the PANI surface more than pure PANI, PANI/PVDF and PANI/PTFE, indicating higher electronegativity than pure PANI, PANI/PVDF, and PANI/PTFE, indicating an increase in the reactivity with interaction of PANI and polymer binders together.

In PANI/G/PVDF/PTFE composite, there was a redistribution of electronic charges on its surface and on F atoms of the polymer binders, with an increase in the density of the red color around the PANI surface from the site of G interaction more than in PANI/G/PVDF and PANI/G/PTFE composites, indicating more electronegativity than PANI/G/PVDF and PANI/G/PTFE composites, thus showing an increase in the reactivity of PANI/G/PVDF/PTFE composite more than that of PANI/G/PVDF and PANI/G/PTFE composites.



**Fig. 6** B3LYP/LanL2DZ calculated MESP for **a-** PANI/G, **b-** PANI/PVDF, **c-** PANI/G/PVDF, **d-** PANI/PTFE, **e-** PANI/G/PTFE, **f-** PANI/PVDF/PTFE and **g-** PANI/G/PVDF/PTFE

## 4 Conclusion

The interaction between both PANI and G, along with the polymer binders PVDF and PTFE, was studied using molecular modeling at DFT:B3LYP/LanL2DZ level. The calculated physical properties, such as TDM and  $\Delta E$  led to the following conclusions:

From the TDM calculations, the TDM of PANI increased from 3.994 Debye with the interaction with polymer binder to be 6.977, 10.569, 11.229 Debye for PANI/PTFE, PANI/PVDE, PANI/PVDF/PTFE, respectively, and  $\Delta E$  of PANI decreased from 4.353 eV to 4.130, 4.092, and 3.979 eV for PANI/PVDE, PANI/PTFE, and PANI/PVDF/PTFE, respectively. TDM of PANI/G composite increased from 3.039 Debye by interacting with polymer binders to be 6.010, 9.012, and 9.822 Debye for PANI/G/PTFE, PANI/G/PVDF/PTFE, and PANI/G/PVDE, respectively, while  $\Delta E$  decreased from 3.236 eV to 3.507, 3.095, 2.127 eV for PANI/G/PTFE, PANI/G/PVDE, and PANI/G/PVDF/PTFE, respectively. From the MESP maps, the reactivity of the PANI/G composite was enhanced with the interaction by the polymer binders PVDF and PTFE, as they caused more redistribution of the electronic charges than PANI/G when forming PANI/G/PVDF, PANI/G/PTFE, and PANI/G/PVDF/PTFE composites.

Correlating the obtained results together, one can conclude that the PANI/G/PVDF/PTFE composite is more suitable than other studied composites as it has the lowest  $\Delta E$ , thus higher reactivity, higher electronegativity, and conductivity, as well as enhancing the electrode's cyclic stability. Therefore, PANI/G/PVDF/PTFE composite is more suitable as an electrode material that can be used in many applications, such as supercapacitors.

Finally, this work indicated that DFT:B3LYP/LanL2DZ is a good computational method, providing good results to follow up on the enhancement in the electronic properties of PANI/G in the presence of the two polymer binders PVDF and PTFE in an appropriate computational time.

**Author contributions** Authors equally contributed to this work.

**Funding** Open access funding provided by The Science, Technology & Innovation Funding Authority (STDF) in cooperation with The Egyptian Knowledge Bank (EKB). There is no funding received.

**Data availability** The data will be available upon request. Contact Medhat. A. Ibrahim: medahmed6@yahoo.com.

## Declarations

**Conflict of interest** I declare that the authors have no competing interests as defined by Springer, or other interests that might be perceived to influence the results and/or discussion reported in this paper.

**Ethical approval** This work is not applicable to both human and/or animal studies.

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