Supporting Information for

1D AND 2D HYBRID POLYMERS BASED ON ZINC PHENYLPHOSPHATES: SYNTHESIS, CHARACTERIZATION AND APPLICATIONS IN ELECTROACTIVE MATERIALS

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Inorganic-organic hybrid polymer, 1D architecture, 2D architecture, metal organophosphate, zinc diphenylphosphate, zinc phenylphosphate, negative electrorheological effect

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Details of single-crystal structure analysis of ZnDPhP

The ZnDPhP structure was solved by direct methods and subsequent Fourier–difference synthesis using SHELXS–97 and refined by the full–matrix least squares against \( F^2 \) method with SHELXL–2014 both invoked from the Olex2 program suite. All non–hydrogen atoms were refined anisotropically, whereas hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters set to 1.2 times the \( U_{	ext{iso}} \) of the parent atoms. The studied crystal was merohedrally twinned by a two-fold rotation around [001] axis. The twin ratios were refined to 0.6969(9):0.3031(9). Data were analysed using CrysAlisPRO software.

Notes and references
1 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. Appl. Cryst., 2009, 42, 339.
2 CrysAlisPro: Software for Single-crystal Data Collection and Processing, Rigaku OD, Oxford, England, 2019.

Table S1. Elemental analysis of ZnDPhP, ZnMPhP-H, ZnMPhP-A, ZnMPhP/BnNH₂, ZnMPhP/BnNH₂, and ZnMPhP/TETA samples

| Sample abbreviation | Formula (theoretical values)\(^a\) | Method of synthesis\(^b\) | C (%) | H (%) | N (%) |
|---------------------|----------------------------------|--------------------------|-------|-------|-------|
| ZnDPhP              | \( \text{C}_6\text{H}_{20}\text{O}_6\text{P}_2\text{Zn} \) (C, 51.13; H, 3.58) | TPhP                     | 51.16 | 3.74  | n/a   |
| ZnMPhP-H            | \( \text{C}_6\text{H}_{12}\text{O}_4\text{Zn} \) (C, 28.21, H, 2.76) | n/a                      | 27.66 | 2.66  | n/a   |
| ZnMPhP-A            | \( \text{C}_6\text{H}_{12}\text{O}_4\text{Zn} \) (C, 30.34, H, 2.12) | M2                       | 30.06 | 2.05  | n/a   |
| ZnMPhP/BnNH₂        | \( \text{C}_{10}\text{H}_{18}\text{N}_4\text{O}_4\text{Zn} \) (C, 38.67; H, 5.19; N, 4.51) | n/a                      | 42.69 | 7.17  | 6.71  |
| ZnMPhP/TETA         | \( \text{C}_{15}\text{H}_{18}\text{N}_4\text{O}_4\text{Zn} \) (C, 45.31; H, 4.09; N, 4.06) | n/a                      | 45.47 | 4.23  | 4.20  |

\(^a\) values of carbon, hydrogen and nitrogen contents calculated for the assumed formula. \(^b\) TPhP, HDPhP, and NaDPhP – synthetic routes; M2 – method of synthesis (see Experimental Section).

Table S2. Thermogravimetric data of ZnMPhP-H and ZnDPhP measured in air (oxidative atmosphere) or argon (inert atmosphere)

| Atmosphere | Type of degradation\(^a\) | Degradation step number, \( n \)\(^b\) | \( T_{\text{onset}} \)\(^c\) (°C) | \( T_{\text{inset,n}} \)\(^d\) (°C) | \( T_{\text{max,n}} \)\(^e\) (°C) | \( T_{\text{endset,n}} \)\(^d\) (°C) | \( \Delta m/\% \)\(^f\) (wt%) | \( m_{\text{res,800}}} \)\(^g\) (wt%) |
|------------|--------------------------|---------------------------------|------------------|------------------|-----------------|------------------|-----------------|-----------------|
| ZnMPhP-H   | air, two-step            | 1                               | 68.0             | 100.4            | 111.9           | 124.6            | 7.31            | 58.26           |
|            |                          | 2                               | 260.8            | 372.1            | 392.4           | 410.4            | 34.30           |
| argon      | two-step                 | 1                               | 74.0             | 115.5            | 130.0           | 135.8            | 6.70            | 63.58           |
|            |                          | 2                               | 343.0            | 459.6            | 480.1           | 505.5            | 27.96           |
| ZnDPhP     | air, multistep           | 1                               | 253.0            | 319.4            | 344.5           | 711.8\(^b\)      | na              | 35.68           |
| argon      | multistep               | 1                               | 287.0            | 414.5            | 435.6           | 610.1\(^b\)      | na              | 40.84           |

\(^a\) Refers to the number of steps in which thermal decomposition occurred: two-step – two well-separated steps of weight loss, multistep – many steps of weight loss overlapping with each other. \(^b\) An individual number ascribed to the respective decomposition region. \(^c\) Temperature of the beginning of weight loss (a bend point on the TG curve for the respective decomposition region denoted with its individual index \( n \)). \(^d\) \( T_{\text{inset,n}} \) and \( T_{\text{endset,n}} \) denote the extrapolated onset and endset temperatures derived from the intersection of two tangents (purple, dashed lines in Figures S21 and S22), respectively. \(^e\) \( T_{\text{max,n}} \) – temperature at the maximum decomposition rate for the respective decomposition step. \(^f\) Mass variation during the respective decomposition step (as % of the initial sample mass). \(^g\) Residual mass of the sample measured at 800 °C (as % of the initial sample mass). \(^h\) Refers to the last component in a multistep mass variation and corresponds to the temperature denoted as \( T_{\text{endset}} \) in Figures S22 and S23A.

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Calculations of bond-valence vectors for zinc and phosphorus centers

Bond valences were calculated using the most widely used equation describing the relationship between the bond length \(d_{ij}\) between the i-th and j-th atoms and the valence of this bond \(s_{ij}\):\(^1\)

\[ s_{ij} = \exp\left(\frac{r_{ij} - d_{ij}}{b} - 1\right) \]  

(S1)

where \(r_i\) and \(b\) are empirically determined constants for the given i-j bond. \(r_i\) is equal to the length of a conceptual bond of a unit valence, whereas the parameter \(b\) is generally treated as a 'universal' constant, often taken to be 0.37 Å.\(^1,2\) The following parameters were used in the calculations: \(r_{PO} = 1.617\ \text{Å} \ (b = 0.37\ \text{Å})\),\(^3\) and \(r_{ZnO} = 1.704\ \text{Å} \ (b = 0.37\ \text{Å})\),\(^3\) together with the experimental \(d_{ij}\) values derived from a single-crystal X-ray analysis of ZnDPhP.

According to the bond–valence vector model,\(^4\) the bond between the coordination center i and the more electronegative ligating atom j of \(s_{ij}\) valence can be represented by the bond–valence vector \(v_{ij}\) directed from i to j with a length defined by the following equation:

\[ |v_{ij}| = s_{ij} \times \left[ 1 - (s_{ij} \times Q_i^{-1})\right] \]  

(S2)

where \(Q_i\) is the charge in the core of the central i-th atom. The lengths of the individual bond–valence vectors \(|v_{ZnO}|\) and \(|v_{PO}|\) were calculated by setting the zinc core charge \(Q_{Zn} = 2\) and the phosphorus core charge \(Q_{P} = 5\).

The bond–valence sums \(S_i\) and lengths of the resultant bond–valence vectors \(|v_i|\) for each coordination centers i connected to the ligating oxygen atoms j were calculated according to the following equations:

\[ S_i = \sum_j s_{ij} \]  

(S3)

\[ v_i = \sum_j v_{ij} \]  

(S4)

\[ |v_i| = (v_i \cdot v_i)^{0.5} \]  

(S5)

The calculated values of \(S_i\) and \(|v_i|\) for each crystallographically independent zinc \((i = Zn)\) or phosphorus \((i = P1 \text{ or } P2)\) coordination centers are summarized in Table S3.

Table S3. Bond–valence sum \(S_i\) and length of the resultant bond–valence vector \(|v_i|\) for each crystallographically independent zinc or phosphorus coordination center in ZnDPhP

| Atom i | \(S_i\) | \(|v_i| \) (v.u.)\(^a\) |
|--------|--------|------------------|
| Zn     | 2.18   | 0.034            |
| P1\(^b\) | 5.02   | 0.062            |
| P2\(^b\) | 4.97   | 0.057            |

\(^a\) valence units.

Notes and references

1 I. D. Brown and D. Altermatt, Acta Crystallogr., Sect. B: Struct. Sci., 1985, 41, 244.
2 N. E. Brese and M. O’Keeffe, Acta Crystallogr., Sect. B: Struct. Sci., 1991, 47, 192.
3 I. Brown, Accumulated Table of Bond Valence Parameters, https://www.iucr.org/__data/assets/file/0007/126574/bvparm2016.cif (accessed Dec 6, 2019) .
4 J. Zachara, Inorg. Chem., 2007, 46, 9760

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Table S4. Cell parameters \((a\ and\ c)\) and cell volume \((V)\) calculated from the PXRD patterns collected during heating of the ZnDPhP sample from 27 °C to 235 °C

| \(T\) (°C) | \(a\) (Å) | \(c\) (Å) | \(V\) (Å\(^3\)) | \(R_{wp}\) \(^b\) |
|----------|-----------|-----------|----------------|-------------|
| **Low-temperature phase (LT–ZnDPhP)** |
| 27       | 12.93229(13) | 12.6473(9) | 1831.81(13) | 14.8 |
| 40       | 12.9410(2) | 12.649(2) | 1834.5(3) | 14.9 |
| 55       | 12.9566(4) | 12.6530(5) | 1839.51(12) | 15.1 |
| 70       | 12.9706(4) | 12.6550(9) | 1843.80(18) | 15.1 |
| 85       | 12.98468(12) | 12.6589(11) | 1848.37(16) | 15.1 |
| 100      | 13.00132(13) | 12.66125(19) | 1853.45(5) | 15.3 |
| 115      | 13.01838(10) | 12.6635(2) | 1858.65(5) | 15.5 |
| 130      | 13.03494(10) | 12.6651(19) | 1863.6(3) | 15.3 |
| 145      | 13.0552(14) | 12.666(4) | 1869.6(7) | 14.5 |
| 160      | 13.06689(9) | 12.69784(10) | 1879.1(4) | 18.5 |
| **High-temperature phase (HT–ZnDPhP)** |
| 160      | 13.91779(18) | nd | nd | 18.5 |
| 175      | 13.9605(8) | nd | nd | 8.4 |
| 190      | 14.0036(8) | nd | nd | 8.2 |
| 205      | 14.0475(7) | nd | nd | 8.0 |
| 220      | 14.0916(7) | nd | nd | 7.8 |
| 235      | 14.1413(8) | nd | nd | 7.7 |

\(^a\) calculated with the formula \(V = 0.5 \times 3^{0.5} \times a^2 \times c\). \(^b\) weighted-profile \(R\)-factor calculated with the formula \(R_{wp} = 100\% \times \left(\frac{\sum_i w_i[y_i(\text{observed}) - y_i(\text{calculated})]^2}{\sum_i w_i[y_i(\text{observed})]^2}\right)^{0.5}.

A fitting of the experimental data points presented in Table S4 by the least-squares method gives the following equations (in which \(T\) is expressed in K) for \(a, c\) and \(V\)– data point from a transition region (denoted as \(B\) in Figure 3) was excluded:

**for the LT–ZnDPhP phase**

\[
\begin{align*}
a(T)_{\text{LT–ZnDPhP}} & = 12.615(10) \, \text{Å} + 10.41(27) \times 10^{-4} \, (\text{Å·K}^{-1}) \, T \\
\left( R^2 = 0.9955 \right) & \quad (S6) \\
c(T)_{\text{LT–ZnDPhP}} & = 12.5973(34) \, \text{Å} + 16.8(10) \times 10^{-5} \, (\text{Å·K}^{-1}) \, T \\
\left( R^2 = 0.9789 \right) & \quad (S7) \\
V(T)_{\text{LT–ZnDPhP}} & = 1734.2(24) \, \text{Å}^3 + 32.1(7) \times 10^{-2} \, (\text{Å}^3 \cdot \text{K}^{-1}) \, T \\
\left( R^2 = 0.9970 \right) & \quad (S8)
\end{align*}
\]

**for the HT–ZnDPhP phase**

\[
\begin{align*}
a(T)_{\text{HT–ZnDPhP}} & = 12.616(23) \, \text{Å} + 30.0(5) \times 10^{-3} \, (\text{Å·K}^{-1}) \, T \\
\left( R^2 = 0.9992 \right) & \quad (S9)
\end{align*}
\]
Table S5. Cell parameters (a and c) and cell volume (V) calculated from the PXRD patterns collected during cooling of the ZnDPhP sample from 235 °C to 27 °C

| T (°C) | a (Å)     | c (Å)     | V (Å³)     | Rwp b |
|--------|-----------|-----------|------------|-------|
|        | Low-temperature phase (LT–ZnDPhP) |           |            |       |
| 27     | 12.9330(5)| 12.6069(8)| 1826.14(19)| 6,5   |
| 40     | 12.94947(15)| 12.6077(5)| 1830.93(9) | 5,0   |
| 55     | 12.9644(3) | 12.6143(7)| 1836.12(14)| 6,1   |
| 70     | 12.98355(8)| 12.623(7) | 1842.8(11) | 6,0   |
| 85     | 13.0053(12)| 12.6381(18)| 1851.2(4) | 5,9   |
| 100    | 13.0242(4) | 12.642(3) | 1857.2(4) | 5,8   |
|        | High-temperature phase (HT–ZnDPhP) |           |            |       |
| 85     | 13.8189(11)| nd        | nd         | 6,5   |
| 100    | 13.8003(4) | nd        | nd         | 5,0   |
| 115    | 13.8481(3) | nd        | nd         | 6,1   |
| 130    | 13.8896(3) | nd        | nd         | 6,0   |
| 145    | 13.9381(3) | nd        | nd         | 5,9   |
| 160    | 13.9776(3) | nd        | nd         | 5,8   |
| 175    | 14.0256(3) | nd        | nd         | 5,7   |
| 190    | 14.0683(3) | nd        | nd         | 5,7   |
| 205    | 14.1037(3) | nd        | nd         | 5,6   |
| 220    | 14.1334(3) | nd        | nd         | 5,5   |
| 235    | 14.1406(7) | nd        | nd         | 5,6   |

a calculated with the formula \( V = 0.5 \times 3^{0.5} \times a^{2} \times c \). b weighted-profile R-factor calculated with the formula \( R_{wp} = 100\% \times \left[ \sum w_i [y_i(\text{observed}) - y_i(\text{calculated})]^2 / \sum w_i [y_i(\text{observed})]^2 \right]^{-0.5} \)

A fitting of the experimental data points presented in Table S5 by the least–squares method gives the following equations (in which \( T \) is expressed in K) for \( a, c \) and \( V \)– data points from a transition region (denoted as \( B' \) in Figure 3) were excluded:

for the LT–ZnDPhP phase

\[
\begin{align*}
a(T)_{LT-ZnDPhP} &= 12.586(13) \text{ Å} + 11.6(4) \times 10^{-4} (\text{Å·K}^{-1}) T \\
c(T)_{LT-ZnDPhP} &= 12.489(26) \text{ Å} + 3.8(8) \times 10^{-5} (\text{Å·K}^{-1}) T \\
V(T)_{LT-ZnDPhP} &= 1710.9(51) \text{ Å}^3 + 3.83(16) \times 10^{-1} (\text{Å}^3\cdot\text{K}^{-1}) T
\end{align*}
\]

\( R^2 = 0.9976 \) (S10)  \( R^2 = 0.9212 \) (S11)  \( R^2 = 0.9967 \) (S12)

for the HT–ZnDPhP phase

\[
\begin{align*}
a(T)_{HT-ZnDPhP} &= 12.86(6) \text{ Å} + 2.58(13) \times 10^{-2} (\text{Å·K}^{-1}) T \\
V(T)_{HT-ZnDPhP} &= 1347.9(19) \text{ Å}^3 + 1.15(6) \times 10^{-1} (\text{Å}^3\cdot\text{K}^{-1}) T
\end{align*}
\]

\( R^2 = 0.9832 \) (S13)

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Determination of the volumetric ($\beta_V$) and linear thermal expansion coefficients

The equations $S6$–$S13$ obtained on the basis of the experimental VT-PXRD data can be utilized for the calculation of both the linear thermal expansion coefficient along the $a$- and $c$-axes of ZnDPhP ($\alpha_L$, where $L = a$ and $c$, respectively) and the volumetric thermal expansion coefficient ($\beta_V$). More specifically, the slopes of the straight lines described by those equations can give the values of $\alpha_L$ or $\beta_V$ since they are defined as:\textsuperscript{1,2}

$$\beta_V = (V_{\text{ref}})^{-1} \times (dV/dT) \quad (S14)$$

$$\alpha_L = (L_{\text{ref}})^{-1} \times (dL/dT) \quad (S15)$$

where $V_{\text{ref}}$ and $L_{\text{ref}}$ are a given unit cell volume (reference volume) and a given lattice parameter (reference length) in some particular crystallographic direction (the $a$, $b$- or $c$-axis direction), respectively. Note that $V_{\text{ref}}$ and $L_{\text{ref}}$ are estimated at some chosen reference temperature ($T_{\text{ref}}$) and in our studies those were the values of the ZnDPhP unit cell parameters ($a$, $c$ and $V$) measured at the lowest temperature within the region subjected to fitting: 27 °C (300.15 K) for LT–ZnDPhP in both measurement modes, or 175 °C (448.15 K) and 115 °C (388.15 K) for HT–ZnDPhP in a heating and cooling mode, respectively. The calculated values of thermal expansion coefficients are summarized in Table S6.

### Table S6. Coefficients of the volumetric and linear thermal expansion of different ZnDPhP crystal phases

| Crystal phase | LT–ZnDPhP | HT–ZnDPhP |
|---------------|-----------|-----------|
|               | $\alpha_a$ (K$^{-1}$) | $\alpha_c$ (K$^{-1}$) | $\beta_V$ (K$^{-1}$) | $T$ range * (K) | $\alpha_a$ (K$^{-1}$) | $T$ range * (K) |
| Heating mode  | 8.05(21) $\times 10^{-5}$ | 13.3(8) $\times 10^{-6}$ | 17.5(4) $\times 10^{-5}$ | 300.15–418.15 | 21.47(35) $\times 10^{-5}$ | 448.15–508.15 |
| Cooling mode  | 8.94(31) $\times 10^{-5}$ | 3.17(7) $\times 10^{-5}$ | 21.0(9) $\times 10^{-5}$ | 300.15–343.15 | 18.6(10) $\times 10^{-5}$ | 388.15–508.15 |

*temperature range over which the respective thermal expansion coefficients were estimated for each ZnDPhP crystal phase.

### Notes and references

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2 S. I. Sadovnikov, A. I. Gusev, A. V. Chukin and A. A. Rempel, *Phys. Chem. Chem. Phys.*, 2016, **18**, 4617.
Table S7. Parameters applied in a calculation of sheet electrical resistance ($\sigma_{sh}$) of the PVDF/(ZnDPhP pyrolyzate) composites based on the four-point probe measurements$^a$

| ZnDPhP pyrolyzate content (wt%) | Thickness of the sample, $t$ (mm) | $R_{\text{slope}}^b$ ($\Omega/\Omega$) | $F_d^c$ | $F_t^d$ |
|----------------------------------|----------------------------------|-----------------------------------|--------|--------|
| 95                               | 1.272                            | 37.198(7)                         | 0.9513 | 0.7849 |
| 90                               | 0.914                            | 22.500(0)                         | 0.9513 | 0.8728 |
| 75                               | 0.849                            | 19.300(3)                         | 0.9513 | 0.8879 |
| 50                               | 0.741                            | 62.999(2)                         | 0.9513 | 0.9117 |

$^a$ in-line probe geometry, with the distance between the adjacent tips (a probe spacing, $s$) of 1 mm. $^b$ the resistance derived from the slope of the $U=f(I)$ curve obtained as a result of the 4PP experiment. $^c$ geometric correction factor accounting for the diameter of the sample ($d = 13$ mm) calculated according to the equation S16. $^d$ geometric correction factor accounting for the thickness of the sample calculated according to the equation S17.

Equations describing the geometric correction coefficients used for the calculation of the sheet electrical resistance$^1$

$$F_d = \ln 2 \times \left\{ \ln 2 + \ln \left( \left( d^2 \times s^{-2} + 3 \right) \times \left( d^2 \times s^{-2} - 3 \right)^{-1} \right) \right\}^{-1} \quad (S16)$$

$$F_t = \ln 2 \times \left\{ \ln \left[ \sinh \left( t \times s^{-1} \right) \times \sinh^{-1} \left( t \times 0.5 \times s^{-1} \right) \right] \right\}^{-1} \quad (S17)$$

where $t$ and $d$ are the thickness and diameter of the circular sample, respectively, whereas $s$ refers to the distance between each tip of the probe (a probe spacing). In our experiments the parameters $d$ and $s$ were constant and equaled to 13 mm and 1 mm, respectively.

Notes and references
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**Figure S1.** Schematic representation of the custom-made system used during crosslinking of silicone rubber composites with or without application of an electric field.
Figure S2. Image and schematic representation of the measurement system used during the electrorheological analysis of the crosslinked silicone rubber composites.

Figure S3. FTIR spectra of ZnDPhP samples synthesized by different methods: (a) HDPhP and (b) TPhP synthetic method.

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Figure S4. PXRD patterns of ZnDPPh (a) calculated from the data obtained in a single-crystal X-ray analysis carried out at 100.0(3) K, as well as measured at room temperature for the samples synthesized from: (b) HDPhP and (c) TPhP. The symbol of ♦ refers to a signal of diamond, which was used as an internal standard.

Figure S5. SEM image of ZnDPPh synthesized according to the TPhP method.

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Figure S6. SEM images of ZnMPhP–H.
Figure S7. FTIR spectra of: (a) ZnMPhP–H, (b) ZnMPhP–A (sample prepared under normal pressure, according to Method M2 – see the Experimental section), (c) ZnMPhP–A after 11 days of exposure to water vapor from air (at room temperature), (d) ZnMPhP–A after 3 days of mixing with liquid water and application of the same drying procedure as in the case of ZnMPhP–H.

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Figure S8. Thermogravimetric (TG) analysis of ZnMPhP–H coupled with quadrupole mass spectrometry (QMS) of the evolved gases: (A) TG, DTG and Total Ion Current (TIC) profiles, (B, C) QMS spectra obtained at selected temperature, (D, E) TG profile (black line) and QMS curves (colored lines) for the ions characteristic for: water ($m/z = 17$ and 18) and phenol ($m/z = 65, 66$ and 94). Abbreviations: $T_{b,1}, T_{b,2} \cong$ temperature of the beginning of weight loss (bend point on the TG curve); $T_{\text{max},1}, T_{\text{max},2} \cong$ temperature at the maximum decomposition rate; $T_{\text{onset},1}, T_{\text{onset},2}$ and $T_{\text{endset},1}, T_{\text{endset},2}$ denote the extrapolated onset and endset temperatures derived from the intersection of two tangents (purple, dashed lines), respectively.

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Figure S9. SEM images of ZnMPhP–A.

Figure S10. $^{31}$P CP/MAS NMR spectra of ZnMPhP–H, ZnMPhP–A and the product of a complete hydrolysis of the phosphoester bonds identified as zinc phosphate tetrahydrate. The spectra were recorded at room temperature. The sidebands are marked with dark blue asterisks, whereas integrals are indicated in light blue.

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Figure S11. PXRD patterns of: ZnMPhP–H, ZnMPhP–A (sample prepared under normal pressure, according to Method M2 – see the Experimental section), ZnMPhP–A after 11 days of exposure to water vapor from air (at room temperature) (denoted as ZnMPhP–A/air) and ZnMPhP–A after 3 days of mixing with water (denoted as ZnMPhP–A/H_2O).

Figure S12. PXRD patterns of the product obtained during a hydrothermal conditioning of ZnMPhP–H (black line), as well as Zn₃(PO₄)₂·4H₂O (hopeite) standard (Powder Diffraction File No. 33-1474, blue bars).

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**Figure S13.** PXRD patterns of the zinc phenylphosphate/amine intercalates obtained from ZnMPhP–A and: n-butylamine (ZnMPhP/BuNH₂) or benzylamine (ZnMPhP/BnNH₂).

**Figure S14.** FTIR spectra of the zinc phenylphosphate/amine intercalates containing: (a) n-butylamine (ZnMPhP/BuNH₂) or (b) benzylamine (ZnMPhP/BnNH₂).

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Figure S15. ZnDPhP crystal structure: (a) ZnDPhP asymmetric unit, (b) single ZnDPhP chain, (c) packing of the adjacent ZnDPhP chains in its unit cell (green, solid lines indicate borders of the unit cell). The view is down the crystallographic $b$-axis (a) or $c$-axis (b, c). For the clarity of presentation all hydrogen atoms were omitted.

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Figure S16. Resultant bond–valence vectors at phosphorus centers (in dark grey) in ZnDPhP chain. For the graphical presentation, it was assumed that 1 v.u. is equal to 10 Å, and the carbon and hydrogen atoms were omitted.
Figure S17. $^{31}$P CP/MAS NMR spectra of ZnDPhP crystals recorded at selected temperatures. The sidebands are marked with black asterisks.
Figure S18. DSC trace of ZnDPhP. The 1st heating (red), cooling (blue) and 2nd heating curves are presented. Enthalpies of the first-order transitions are given in parentheses.

Figure S19. VT-PXRD patterns of ZnDPhP measured in a heating mode (from 27 °C to 235 °C) at 3 selected temperatures: 145 °C (blue line), 160 °C (green line), and 175 °C (red line).

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Figure S20. VT-PXRD patterns of ZnDPhP measured in a cooling mode (from 235 °C to 27 °C) at 4 selected temperatures: 70 °C (blue line), 85 °C (green line), 100 °C (orange line), and 115 °C (red line).

Figure S21. TG (green line) and DTG (black line) profiles of ZnMPhP–H collected in air at a heating rate of 10 °C min⁻¹. T_onset and T_endset denote the extrapolated onset and endset temperatures derived from the intersection of two tangents (purple, dashed lines), respectively. The blue arrows indicate temperature of the beginning of weight loss (Tb, a bend point on the TG curve) during the respective decomposition step. The numbers in subscripts refer to the consecutive degradation regions.
Figure S22. TG (green line) and DTG (black line) profiles of ZnDPhP collected in air at a heating rate of 10 °C min⁻¹. $T_{\text{onset}}$ and $T_{\text{endset}}$ denote the extrapolated onset and endset temperatures derived from the intersection of two tangents (purple, dashed lines), respectively. The blue arrows indicate temperature of the beginning of weight loss ($T_b$, a bend point on the TG curve) during the respective decomposition step. The numbers in subscripts refer to the consecutive degradation regions.
Figure S23. Thermogravimetric (TG) analysis of ZnDPhP coupled with quadrupole mass spectrometry (QMS) of the evolved gases: (A) TG, DTG and Total Ion Current (TIC) profiles, (B, C) QMS spectra obtained at selected temperature, (D) TG profile (black line) and QMS curves (colored lines) for the ions characteristic for phenol. Abbreviations: $T_{b,1}$ – temperature of the beginning of weight loss (a bend point on the TG curve); $T_{\text{max},1}$ – temperature at the maximum decomposition rate; $T_{\text{onset},1}$ – the extrapolated onset temperature for the first degradation step derived from the intersection of two tangents (purple, dashed lines); $T_{\text{endset}}^*$ – the extrapolated endset temperature for the last degradation step derived from the intersection of two tangents (purple, dashed lines).

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Figure S24. PXRD pattern of the solid residue obtained in the course of ZnMPhP–H thermal degradation carried out for 6 h in argon at 600 °C (black line). Reflexes characteristic of zinc phosphate (Powder Diffraction File No 29–1390) and zinc pyrophosphate (Powder Diffraction File No 39–0711) are indicated with the colored bars: blue for Zn₃(PO₄)₂ and red for Zn₂P₂O₇.

Figure S25. PXRD pattern of the solid residue obtained in the course of ZnDPhP thermal degradation carried out for 6 h in argon at 600 °C (black line). Reflexes characteristic of zinc pyrophosphate (Powder Diffraction File No 39–0711) and zinc metaphosphate (Powder Diffraction File No 30–1488) are indicated with the colored bars: blue for Zn(PO₃)₂ and red for Zn₃P₂O₇.

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Figure S26. Raman spectra of the solid residues obtained in the course of ZnMPhP–H thermal degradation carried out: (a) for 6 h in air at 600 °C (blue lines) and (b) for 6 h in argon at 600 °C (red lines). As insets the 2000 cm$^{-1}$–800 cm$^{-1}$ regions of Raman spectra after baseline correction are presented: $D/G$ denotes a ratio of the $D$ band intensity to the $G$ band intensity.

Figure S27. Raman spectra of the solid residues obtained in the course of ZnDPhP thermal degradation carried out: (a) for 6 h in air at 600 °C (blue lines) and (b) for 6 h in argon at 600 °C (red lines). As insets the 2000 cm$^{-1}$–800 cm$^{-1}$ regions of Raman spectra after baseline correction are presented: $D/G$ denotes a ratio of the $D$ band intensity to the $G$ band intensity.

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Figure S28. Electrorheology. Viscosity curves measured under different values of an electric field for the PDMS100-based dispersion containing 20 wt% ZnDPhP. The measurements were conducted at 20 °C.
Figure S29. Electrorheology. Viscosity curves measured under different values of an electric field for the PDMS100-based dispersion containing 20 wt% ZnMPH–H. The measurements were conducted at 20 °C.
Figure S30. Electrorheology. Viscosity curves measured under different values of an electric field for the PDMS100-based dispersion containing 20 wt% ZnMPhP-A. The measurements were conducted at 20 °C.
Figure S31. Impact of the cyclic changes in the electric field strength \( E_1 \) and \( E_2 \) on the storage modulus \( G' \), presented as solid shapes) and normal force \( F_N \), presented as solid lines) of the cured PDMS (■) and its 1-wt% composites containing ZnDPhP (♦, ●) or ZnMPhP–A (▲, ▼). Before the measurements the samples were cured at 2 different values of the electric field strength \( E_{\text{curing}} \). The EF–time profile applied during the measurements is depicted as a red, solid line.
Figure S32. Impact of the cyclic changes in the electric field strength ($E_1$ and $E_2$) on the loss modulus ($G''$, presented as solid shapes) and damping factor [$\tan(\delta)$, presented as solid lines] of the cured PDMS (■) and its 1-wt% composites containing ZnDPhP (♦, ●) or ZnMPhP–A (▲, ▼). Before the measurements the samples were cured at 2 different values of the electric field strength ($E_{\text{curing}}$). The EF–time profile applied during the measurements is depicted as a red, solid line.