

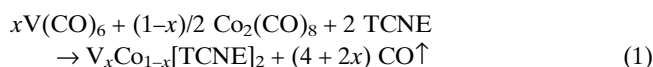
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Control of Coercivity in Organic-Based Solid Solution V_xCo_{1-x}[TCNE]₂·zCH₂Cl₂ Room Temperature Magnets**

By Konstantin I. Pokhodnya, Vladimir Burtman, Arthur J. Epstein, James W. Raebiger, and Joel S. Miller*

The reaction of tetracyanoethylene (TCNE) with V(CO)₆ forms a magnet of nominal V[TCNE]₂·zCH₂Cl₂ (y ~ 2; z ~ 0.3) composition with a magnetic ordering temperature (T_c) exceeding room temperature.^[1] Recently, using these volatile precursors, a chemical vapor deposition (CVD) route to solvent-free thin films of the V[TCNE]₂ magnet with enhanced

air stability was developed.^[2] V[TCNE]₂ is an amorphous, disordered material with a small coercive field, H_{cr} < 1 Oe at room temperature and 7.4 Oe at 5 K.^[3] It is a magnetic semiconductor with a room temperature conductivity of ~ 10⁻⁴ S/cm, and recent magnetotransport studies indicate that electrons in the valence and conducting bands are spin polarized suggesting "spintronic" applications.^[4] Use of other metal carbonyls to form magnetic materials with TCNE has only been successful for Fe[TCNE]₂ (T_c = 100 K).^[5] The reaction of TCNE and Co₂(CO)₈, albeit fast, does not lead to a material that magnetically orders.^[5] In contrast with the slow reaction of TCNE and Fe(CO)₅, the fast reactions of TCNE with either V(CO)₆ or Co₂(CO)₈ suggest that solid solutions of V_xCo_{1-x}[TCNE]₂ exhibiting unique properties distinct from those for x = 0 or 1 might be attainable. The presence of Co^{II} with its large magnetocrystalline anisotropy^[6] should lead to an enhanced coercivity.^[7] Thus, with the goal of enhancing the coercivity needed for some spintronic^[8] and other applications, V_xCo_{1-x}[TCNE]₂ powders of nominal (0 < x < 1) compositions, were prepared from CH₂Cl₂, via Equation 1,



and their infrared and magnetic properties were investigated to assure that solid solutions with different properties, and not physical mixtures, had formed. Herein we report the results of preliminary study of V_xCo_{1-x}[TCNE]₂·zCH₂Cl₂ (0 < x < 1) and compare its magnetic properties to that of a physical mixture of similar composition.

The ν_{C≡N} IR spectra of the dichloromethane solvates of Co[TCNE]₂, V[TCNE]₂, and solid solutions of V_xCo_{1-x}[TCNE]₂ (0 < x < 1) composition are consistent with the formation of solid solutions, and are inconsistent with a physical mixture. The ν_{C≡N} region for the physical mixture is the superposition of the ν_{CN} absorptions for Co[TCNE]₂·zCH₂Cl₂ (2112, 2171, 2224 cm⁻¹)^[9] and V[TCNE]₂·zCH₂Cl₂ (broad absorption at 2090 cm⁻¹ and three relatively narrow features at 2152, 2191, 2214 cm⁻¹).^[1a,3] In contrast, solid solutions exhibit a family of spectra (Fig. 1), in which, as x decreases, i) the broad 2090 cm⁻¹ feature becomes narrower and shifts towards 2112 cm⁻¹, ii) the peak at 2152 cm⁻¹ shifts towards 2171 cm⁻¹, iii) the peak at 2191 cm⁻¹ broadens and merges into the high energy side of the broad absorption at 2171 cm⁻¹ x < 0.5, and finally, iv) the feature at 2214 cm⁻¹ shifts to 2224 cm⁻¹. Hence, the gradual transformation of absorptions with decreasing x is inconsistent with phase separation, implying that the correlated peaks have the same origin for V[TCNE]₂·zCH₂Cl₂ and Co[TCNE]₂·zCH₂Cl₂.

The temperature dependence of the zero field cooled (ZFC) magnetization, M(T), of the solid solution V_xCo_{1-x}[TCNE]₂·zCH₂Cl₂ (0 < x < 1) in the range of 5–400 K (Fig. 2), exhibits similar features, and all magnetically order above 280 K for x > 0.05. The magnetization measured at 5 Oe is relatively small at low temperatures, increases upon warming, reaches a maximum, and then decreases with a different slope

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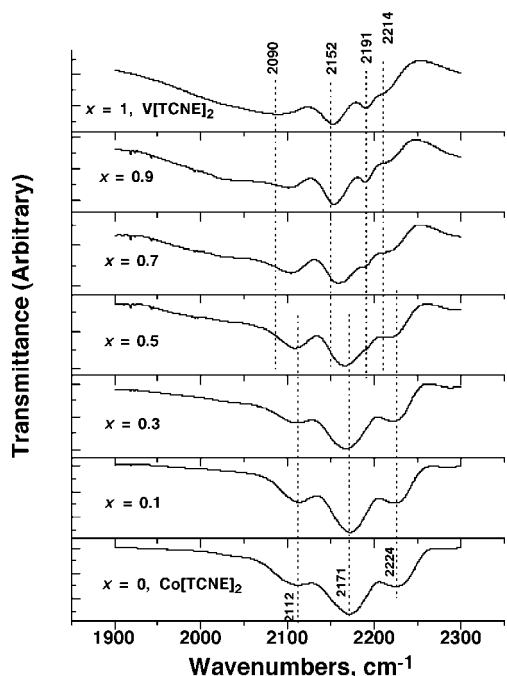


Fig. 1. ν_{CN} IR spectra of $\text{V}_x\text{Co}_{1-x}[\text{TCNE}]_2 \cdot z\text{CH}_2\text{Cl}_2$ ($0 \leq x \leq 1$).

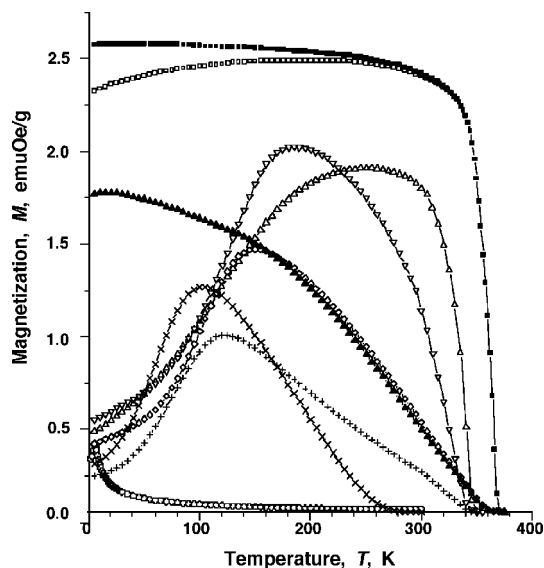


Fig. 2. Temperature dependence of the field-cooled (FC) $M(H)$ for $\text{V}_x\text{Co}_{1-x}[\text{TCNE}]_2 \cdot z\text{CH}_2\text{Cl}_2$ ($x = 1$, \blacksquare ; $x = 0.5$, \blacktriangle), and ZFC $M(H)$ for solid solutions of $\text{V}_x\text{Co}_{1-x}[\text{TCNE}]_2 \cdot z\text{CH}_2\text{Cl}_2$ ($0 < x < 1$) ($x = 1$, \square ; $x = 0.9$, \triangle ; $x = 0.7$, ∇ ; $x = 0.5$, \diamond ; $x = 0.3$, $+$; $x = 0.1$, \times ; and $x = 0$, \circ). Data were collected in 5 Oe external magnetic field except $\text{Co}[\text{TCNE}]_2 \cdot z\text{CH}_2\text{Cl}_2$ for which 500 Oe field was used.

that increases with increasing x . The temperature of the maximum in $M(T)$, T_{max} , shifts from ~ 250 to 100 K as x decreases from 0.9 to 0.1, but the onset of the magnetic transitions is reduced a little from 370 to 355 K for $x \geq 0.3$ and shifts to 280 K for $x \sim 0.1$. FC $M(T)$ for $\text{V}[\text{TCNE}]_2 \cdot z\text{CH}_2\text{Cl}_2$ ($x = 1$) is practically temperature independent below ~ 350 K, and on further warming it drops abruptly as a magnetic transition takes place with its onset at 370 K (Fig. 2) in agreement

with that reported for $\text{V}[\text{TCNE}]_2 \cdot z\text{CH}_2\text{Cl}_2$.^[3] $\text{Co}[\text{TCNE}]_2 \cdot 0.4(\text{CH}_2\text{Cl}_2)$, made from $\text{Co}_2(\text{CO})_8$, is paramagnetic at room temperature with a moment of $4.72 \pm 0.05 \mu_{\text{B}}$ that exceeds the spin-only value of $4.58 \mu_{\text{B}}$ as is expected for high-spin Co^{II} and two $S = 1/2$ $[\text{TCNE}]^{\cdot -}$ radicals. Below 100 K the magnetic moment rapidly decreases upon cooling, suggesting a strong antiferromagnetic coupling.

Partial substitution of V in $\text{V}[\text{TCNE}]_2$ by Co introduces a substantial structural disorder, which manifests itself by a pronounced irreversibility of magnetic properties as $M_{\text{ZFC}} \neq M_{\text{FC}}$. It rapidly increases upon cooling below T_{max} , reminiscent of a spin-glass behavior.^[10a] At 5 K the FC magnetization for the $x = 0.5$ solid solution is more than 20 times higher than the ZFC value (Fig. 2), in contrast to a small irreversibility observed for $\text{V}[\text{TCNE}]_2 \cdot z\text{CH}_2\text{Cl}_2$ ($< 10\%$ at 5 K), attributed to the presence of CH_2Cl_2 .^[2]

The temperatures dependencies of the in-phase (χ') and out-of-phase (χ'') components of the complex AC (alternating current) susceptibility for the $x = 0.5$ solid solution display a broad peak at 150 and 120 K (10 Hz), respectively, similar to that in DC (direct current) measurements (Fig. 3). The temperature of the maximum in both $\chi'(T)$ (T_f) and $\chi''(T)$ gradually increases with increasing frequency, indicating a presence of time-dependent relaxation processes that are characteristic

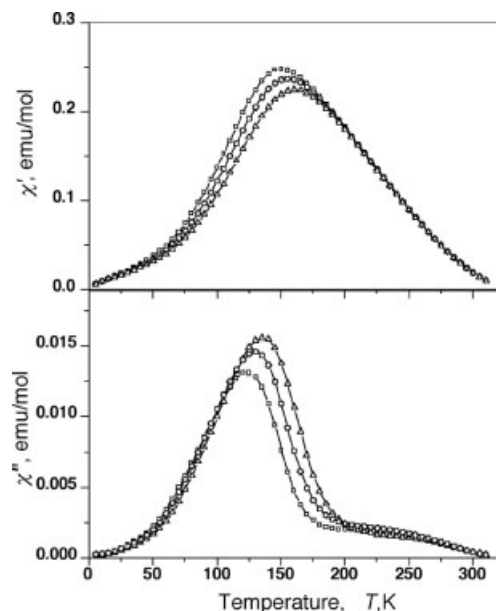


Fig. 3. $\chi'(T)$ and $\chi''(T)$ for $\text{V}_x\text{Co}_{1-x}[\text{TCNE}]_2 \cdot z\text{CH}_2\text{Cl}_2$ ($x \sim 0.5$) in $H_{\text{ac}} = 1$ Oe at 10 Hz (\square), 100 Hz (\circ), and 1000 Hz (\triangle).

for spin-glasses.^[10b] Interestingly, the normalized frequency shift of T_f per frequency (ω) decade, $\Delta T_f/[T_f \Delta(\log \omega)]$, is ~ 0.03 , which is an order of magnitude lower than this value for superparamagnets.^[10c]

Above T_{max} , $\chi''(T)$ decreases more rapidly than $\chi'(T)$, indicating an abrupt change in the magnetic irreversibility. Around 200 K it reaches a plateau at $\sim 15\%$ of its value at T_{max} . In this region $\chi''(T)$ does not have a frequency depen-

dence, and above 250 K it starts to decrease, approaching zero around 330 K. This complex behavior suggests that at least two temperature regions where significant changes in $\chi''(T)$ occur.

The enhanced disorder in $V_xCo_{1-x}[TCNE]_2 \cdot zCH_2Cl_2$ due to the presence of Co^{II} also reveals itself in the magnetization field dependence, $M(H)$ (Fig. 4). The $M(H)$ of $V[TCNE]_2 \cdot zCH_2Cl_2$ reaches 95 % of its saturation value at 2000 Oe, as

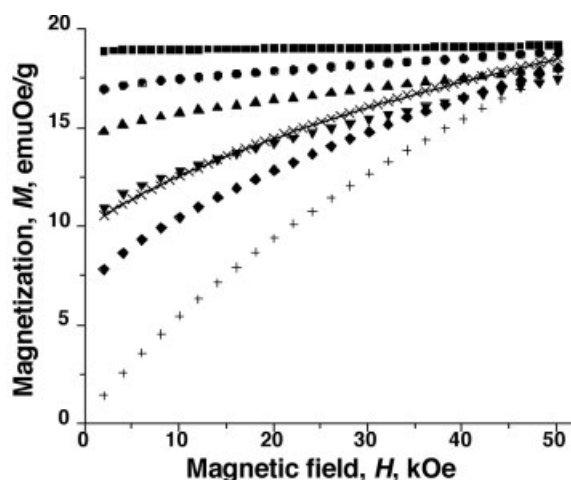


Fig. 4. 5 K $M(H)$ for $V_xCo_{1-x}[TCNE]_2 \cdot zCH_2Cl_2$: $x=1$ (■); $x=0.9$ (●); $x=0.7$ (▲); $x=0.5$ (▼); $x=0.3$ (◆); $x=0$ (+), and a 1:1 physical mixture (×) and a fit to $0.495M_{x=1}(H) + 0.505M_{x=0}(H)$ (solid line).

previously reported.^[3] In contrast, $M(H)$ of paramagnetic $Co[TCNE]_2 \cdot zCH_2Cl_2$ does not saturate, and at 50 kOe it reaches 40 % of the value expected from the Brillouin function consistent with significant antiferromagnetic coupling. The $M(H)$ for physical mixtures can be fitted by the sum of $M(H)$ for pure $M[TCNE]_2 \cdot zCH_2Cl_2$ ($M=V,Co$) compounds as exemplified for $V_xCo_{1-x}[TCNE]_2 \cdot zCH_2Cl_2$ ($x=0.495$) (Fig. 4). In contrast, the $M(H)$ of any of the solid solutions is inconsistent with that of the corresponding physical mixture.

For the solid solutions the $M(H)$ at 2 kOe gradually decreases with increasing of Co content, but saturation is not achieved at 50 kOe consistent with an increase of disorder. For $x < \sim 0.3$ the $M(H)$ resembles that of $Co[TCNE]_2 \cdot zCH_2Cl_2$ ($x=0$), suggesting that for $x < \sim 0.3$ there is a substantial amount of “free” Co^{II} spins, which are only weakly coupled to the magnetic clusters.

$M(H)$ between ± 1 kOe at 5 K reveals hysteretic behavior for both the solid solution and physical mixture of $V_xCo_{1-x}[TCNE]_2 \cdot zCH_2Cl_2$ ($0 < x \leq 1$) (Fig. 5). The coercivity, H_{cr} , increases with increasing Co content (decreasing x), reaching a maxi-

um of 270 Oe for $x=0.3$ and then rapidly decreases (Fig. 5, inset). The latter value is 35 times greater than the 7.4 Oe for the physical mixture and that of $V[TCNE]_2$,^[3] again indicating a lack of a phase separation. At 300 K $H_{cr} \sim 15$ Oe for the $V_xCo_{1-x}[TCNE]_2$ ($x \sim 0.3$), which is more than an order of magnitude higher than this value for $V[TCNE]_2$.^[3] Furthermore, the remanent magnetization of 6.1 emuOe g^{-1} for $x \sim 0.5$ is about 25 times higher than that for $V[TCNE]_2$.^[3]

Partial substitution of V with Co in $V[TCNE]_2 \cdot zCH_2Cl_2$ introduces an additional disorder. Consequently the random site occupancy within a non-crystalline lattice increases the overall randomness and minimizes phase separation. Since $Co[TCNE]_2 \cdot zCH_2Cl_2$ formed from $Co_2(CO)_8$ is paramagnetic and $V[TCNE]_2 \cdot zCH_2Cl_2$ orders magnetically, there should be a critical concentration of V, or effective percolation limit, that provides sufficient magnetic coupling on a microscopic scale that results in high T_c magnetic ordering on a macroscopic scale. Within this model, magnetic ordering requires extended coupling between pairs of V spin sites, via a single $S=1/2 [TCNE]^-$.^[11] Each $[TCNE]^-$ has four CN groups and due to the sp-hybridization of the coordinating lone pair of electrons on each nitrile, each CN can only bond to one M. Each octahedral V site most probably bonds to 6 $[TCNE]^-$ molecules. Hence, to fulfill the stoichiometry, on average each M bonds to two additional Ms resulting in a total of 12 “nearest neighbor” M sites one of which must be V, if Co^{II} does not participate in the magnetic ordering. The experimental results suggest that the percolation limit is below 0.3, as for $x \geq 0.3$ the onset T_c does not change very much. The differences in the shape in $M(T)$ as $T \rightarrow T_c$ is attributed to different concentrations of Co being weakly coupled to the magnetic cluster.

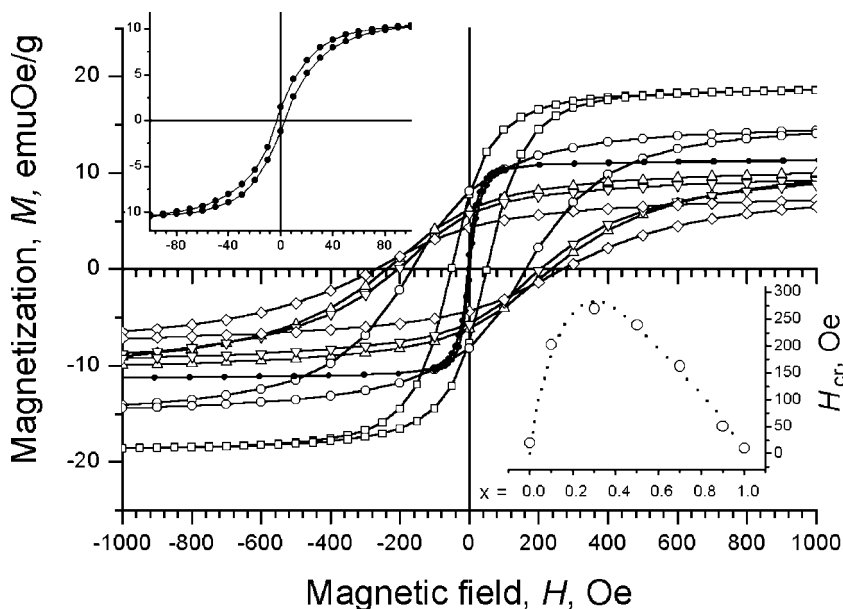


Fig. 5. Hysteresis loops at 5 K for the $V_xCo_{1-x}[TCNE]_2 \cdot zCH_2Cl_2$ ($0.1 \leq x \leq 0.9$) solid solutions ($x=0.9$, □; $x=0.7$, ○; $x=0.5$, △; $x=0.3$, ▽; $x=0.1$, ◇), and physical mixture consisting of $V[TCNE]_2 \cdot zCH_2Cl_2$ and of $Co[TCNE]_2 \cdot zCH_2Cl_2$ in 1:1 ratio (●). The top left inset shows the physical mixture data in a smaller scale, and the bottom right inset shows the coercive field, H_{cr} , dependence upon x (line is a guide for the eye).

The spin-glass phase persists through the percolation limit into the magnetically ordered phase.^[10] At low temperatures the magnetic phase breaks into a number of relatively large, but randomly frozen sub-clusters forming a cluster-glass phase. Hence, the long-range magnetic order is destroyed although magnetic clusters are still present.

That $\chi''(T)$ is sensitive to a magnetic cluster formation supports a "re-entrant" behavior. For $x \sim 0.5$ the first magnetic transition occurs at ~ 330 K. Above 200 K, $\chi'(T)$ is almost frequency independent, suggesting a formation of the finite magnetic phase. Below 200 K $\chi''(T)$ abruptly rises indicating a magnetic transition to a different state. Since $\chi''(T)$ has a frequency dependence characteristic of a spin-glass state, the material re-enters a frozen disordered state. This re-entrant behavior has been observed for the amorphous metallic magnets^[10d] and $\text{Mn}[\text{TCNE}]_2 \cdot z\text{CH}_2\text{Cl}_2$,^[12] and an increase of the random anisotropy arising from an increase of the cobalt content is the main reason of enhanced H_{cr} .

In summary, a family of new solid solution room temperature magnets of $\text{V}_x\text{Co}_{1-x}[\text{TCNE}]_2 \cdot z\text{CH}_2\text{Cl}_2$ ($0 < x < 1$) composition has been characterized. Substitution of Co^{II} for V^{II} in $\text{V}[\text{TCNE}]_2 \cdot z\text{CH}_2\text{Cl}_2$ does not alter T_{c} , however, H_{cr} is enhanced by an order of magnitude indicating a drastic increase of random anisotropy. Hence, the magnetic properties of the room temperature $\text{V}[\text{TCNE}]_2 \cdot z\text{CH}_2\text{Cl}_2$ magnet can be finely tuned via a synthetic organic chemistry methodology, making this material more amenable in future technologies. Preparation and study of solid solution thin film magnets is now in progress.

Experimental

Due to the air/water sensitivity of the materials studied, all manipulations and reactions were performed in a Vacuum Atmospheres DriLab glove box (< 1 ppm O_2 and < 1 ppm H_2O). CH_2Cl_2 was distilled from CaH_2 . $\text{V}(\text{CO})_6$ and $\text{Co}_2(\text{CO})_8$ were sublimed at 40°C and 50 mtorr. TCNE was sublimed at 85°C and 50 mtorr to obtain colorless crystalline material.

In a typical preparation appropriate equivalents of $\text{V}(\text{CO})_6$ and $\text{Co}_2(\text{CO})_8$ (providing in total 0.15 mmol of metals) were each dissolved in 5 mL of CH_2Cl_2 , and then drop-wise added to a stirred filtered solution of TCNE (0.30 mmol) in 10 mL of CH_2Cl_2 , Equation 1. The solution quickly turned dark with the evolution of CO, and was stirred overnight with venting. The dark amorphous product was filtered, washed with CH_2Cl_2 , and dried (yield $\sim 95\%$) [13]. Typical observed elemental analysis (calcd) [14] for $\text{V}_x\text{Co}_{1-x}[\text{TCNE}]_2 \cdot z\text{CH}_2\text{Cl}_2$ [$x \sim 0.51$; $z = 0.53$, $\text{C}_{12.53}\text{H}_{1.06}\text{Cl}_{1.06}\text{Co}_{0.49}\text{V}_{0.51}$; [%] C = 42.39 (42.27), H = 0.40 (0.30), N = 31.39 (31.47), Co = 8.16 (8.11), and V = 7.25 (7.30); ($x \sim 0.18$; $z = 0.54$), $\text{C}_{12.55}\text{H}_{1.10}\text{Cl}_{1.10}\text{Co}_{0.82}\text{N}_8\text{V}_{0.18}$; [%] C = 41.94 (41.89), H = 0.38 (0.30), N = 31.13 (31.17), Co = 13.47 (13.44), and V = 2.64 (2.55)]. Pure $\text{M}[\text{TCNE}]_2 \cdot z\text{CH}_2\text{Cl}_2$ ($\text{M} = \text{V}, \text{Co}$) were prepared in the same way (yield $\sim 95\%$), and physical mixtures of $\text{V}_x\text{Co}_{1-x}[\text{TCNE}]_2 \cdot z\text{CH}_2\text{Cl}_2$ ($x \sim 0.5$) composition were obtained via a gentle mechanical mixing to avoid solid-state reaction. Thermogravimetric analysis (TGA) revealed the presence of $\sim 0.35\text{--}0.55$ CH_2Cl_2 molecules per formula unit for $\text{V}_x\text{Co}_{1-x}[\text{TCNE}]_2 \cdot z\text{CH}_2\text{Cl}_2$ ($0 \leq x \leq 1$).

Powder samples for magnetic measurements were loaded in airtight Delrin holders and packed with oven-dried quartz wool to prevent movement of the sample in the holder. The DC magnetization temperature dependence was obtained by cooling in zero field and then data were collected on warming in 5 Oe external magnetic field using a Quantum Design MPMS-5XL 5 T SQUID magnetometer equipped with a reciprocating sample measurement system, low field option, and continuous low temperature control with enhanced thermometry features. The AC magnetic susceptibility was measured in 1 Oe ac field (zero DC applied field), at 10, 100, and 1000 Hz. Phase sensitive lock-in detection allowed both the in-phase (χ') and out-of-phase (χ'') linear susceptibilities to be

extracted. TGA was performed on a TA Instruments TGA 2050 analyzer. Infrared spectra were obtained using BioRad FTS 40 spectrometer.

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Enhanced Light Extraction from Organic Light-Emitting Diodes with 2D $\text{SiO}_2/\text{SiN}_x$ Photonic Crystals**

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For thin-film organic light-emitting diode (OLED) structures, only a small fraction of total photons generated inside is

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