Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2023

Supporting Information

Synergistic Binding between Engineered Interface and Functionalized Ferrocene offers Remarkable Charge Extraction Efficiency in Lead Halide Perovskites

Monika Ahlawat[#], Santosh Kumari[#], and Vishal Govind Rao^{*}

Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur, 208016, Uttar Pradesh, India

Corresponding Author

* Vishal Govind Rao, Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur, 208016, Uttar Pradesh, India; orcid.org/0000-0003-1205-3006; E-mail: vgrao@iitk.ac.in

[#]Both authors contributed equally to the manuscript.

S1. Experimental methods

Materials: Lead (II) bromide (PbBr₂, Sigma Aldrich, $\geq 98\%$), cesium carbonate (Cs₂CO₃, Sigma Aldrich, 99.9%), oleic acid (OAc, Sigma Aldrich, technical grade, 90%), oleylamine (OAm, Sigma Aldrich, technical grade, 70%), 1-octadecene (ODE, Sigma Aldrich, 90%), toluene (Sigma Aldrich, anhydrous, 99.8%), acetone (Finar), and ethanol (Pharmco-Aaper, HPLC, anhydrous, 200 proof) were used as received without further purification.

Synthesis of CsPbBr₃ nanostructures (CPB): The colloidal synthesis of monodisperse CPB was adapted from the hot-injection protocol as reported by Protesescu et al.¹ First, the Cs-oleate precursor was prepared by dissolving 40.7 mg of Cs₂CO₃ in 2 mL of ODE along with 125 µL of OAc in a 100 mL three-neck round bottom flask at 60 °C. The mixture was dried under nitrogen flow and heated by gradually raising the temperature to 120 °C. After 1 hour, the temperature was raised to 150 °C under an N2 atmosphere to complete the reaction. Next, for preparation of the Pb-oleate, 138.1 mg of PbBr₂, 10 mL of ODE, 1 mL of OAm, and 1 mL of OAc were mixed in another 100 mL three-neck round bottom flask at 100 °C. The mixture was dried under nitrogen flow for 1 hour at an increased temperature of 120 °C. Raising the temperature to 160 °C under an N2 atmosphere, followed by a swift injection of 0.8 mL Csoleate. After 5 s, the reaction mixture was immediately cooled in an ice water bath to quench the reaction, which was observed with a color change from yellow to fluorescent green. To purify the NCs, the crude solution was dissolved in 12 mL acetone and centrifuged at 12000 rpm for 20 min. The supernatant was discarded, and the collected pellet was dispersed in 10 mL of toluene. The supernatant collected from further centrifugation at 4400 rpm for 5 min was stored as stock CPB colloidal solution.

Post-synthetic ligand exchange: To exchange the pristine ligands OAm/OAc with NK-12, 93.76 μ L of 3.3 mM NK-12 solution (prepared in ethanol/toluene mixed solvent) was slowly added to 200 μ L of CPB (1.3 μ M) solution with stirring. The exchanged nanostructures were centrifuged with acetone to remove the free ligands and redispersed in 200 μ L toluene to give a colloidal solution, CPB NK-12.

Preparation of FcS4 sample: 20 mM FcS4 stock solution was prepared by completely dissolving FcS4 in ethanol with sonication and diluting it to 2 mM using ethanol. Before the experiment, a 2 mM ethanol solution of FcS4 was sequentially diluted to 0.2 mM, then to 0.02 mM, and further to 0.002 mM in toluene.

Characterization Methods: Steady-state absorption and photoluminescence (PL) spectra were recorded on a JASCO V770 spectrophotometer and a Horiba Scientific FluoroMax+ spectrofluorometer. All the samples were excited at 365 nm, and the step size was set to 1 nm for all PL measurements.

Powder X-ray diffraction patterns (PXRD) were recorded using a PANalytical X'Pert X-ray diffractometer using Cu-K α X-radiation ($\lambda = 1.54$ Å) at 30 kV and 10 mA power.

Transmission electron microscopy (TEM) images were captured using an FEI-Tecnai G² 12 Twin at 120 kV transmission electron microscope for the morphological characterization of the two different surface chemistry-based CPB dispersed in toluene. High-resolution TEM (HRTEM) measurements were carried out on a Titan G² 60-300 transmission electron microscope operated at 300 kV. To prepare the TEM sample with FcS4, 77.86 nM FcS4 stock solution was mixed with ~12.9 nM colloidal dispersion of each sample in toluene and allowed to equilibrate for 10 minutes. The solution was then drop-casted over a carbon-coated copper grid and dried at room temperature.

Dynamic light scattering (DLS) size measurements were performed using a Malvern Zetasizer Pro ZSU5800 instrument with ~12.9 nM colloidal dispersion of both samples in toluene.

Fourier transform infrared spectroscopy (FTIR) measurements of powder samples were performed using Bruker FTIR spectrophotometer alpha II.

¹H nuclear magnetic resonance spectroscopy (NMR) data were collected using a JEOL JNM-LA 500 MHz spectrometer.

Time-resolved photoluminescence (TRPL) measurements were carried out on a life spec (II) Edinburgh time-correlated single-photon counting (TCSPC) spectrophotometer using a 375 nm pulsed diode laser for excitation. The instrument response function of the setup was ~120 ps, recorded using a diluted solution of Ludox in water. The F900 software provided by Edinburgh Instruments was used to analyze decay curves by the nonlinear least-squares iteration method. The χ^2 values and distribution of the residuals examined the quality of the decay curve fits.

Transient absorption measurements were performed on a Transient absorption spectrometer from Ultrafast Systems, USA. The amplified laser power of 5 mJ/pulse @ 800 nm @ 1kHz was generated from Astrella Amplifier, coherent Inc USA. The pump wavelength was 400 nm 120 nJ@ 500 Hz generated from OperaSolo OPA, Coherent Inc US.

X-ray photoelectron spectroscopy (XPS) surface elemental mapping and binding energy measurements were conducted on a PHI 5000 Versa Probe-II, FEI Inc., Japan, equipped with a monochromatized Al K α (1486.6 eV) radiation source.

S2. CPB concentration calculations

To determine the Concentration of the CPB, firstly molar extinction coefficient (ϵ) at $\lambda = 335$ nm was derived using the method described by De Roo et al.²

$$\varepsilon = \frac{N_A d^3}{ln^{[n]}(10)} \mu_i \tag{1}$$

Using the reported value³ of the intrinsic absorption coefficient (μ_i) of CPB = 1.98×10^5 cm⁻¹ at 335 nm and the average size (*d*) of CPB determined from HRTEM analysis to be 9 nm, molar extinction coefficient (ε) at $\lambda = 335$ nm was calculated as follows:

$$\varepsilon_{335} = 6.022 \times 10^{23} \times 1.98 \times 10^5 \times 9^3 \ cm^{-1} \mu M^{-1} = 37.7622 \ cm^{-1} \mu M^{-1}$$

Further, using the Beer-Lambert law $A = \varepsilon cl$, concentration of CsPbBr₃ was determined as:

$$c = \frac{A_{335}}{\varepsilon_{335}l} = \frac{0.4883}{37.7622 \ cm^{-1}\mu M^{-1} \times 1 \ cm} = 12.9 \ nM$$

Note: The concentration of CPB NK-12 was estimated according to CPB concentration, considering no significant loss during ligand exchange.

S3. Double reciprocal analysis of PL quenching and K_{app} determination

Double reciprocal analysis of PL quenching was done using the modified Benesi-Hildebrand method,^{4,5} originally used for estimating binding constant using absorbance data. The association constant (K_{app}) between the adsorbed quencher molecules and the nanocrystals was determined using the following expression (equation 2). Equation 2 relates normalized PL intensity of unbound (ϕ_0 , without FcS4) and the relative intensity observed after each addition of FcS4 (ϕ_{obs}) to the intensity of the bound state (ϕ') using K_{app} .

$$\frac{\phi_0}{\phi_0 - \phi_{obs}} = \frac{\phi_0}{\phi_0 - \phi} + \frac{\phi_0}{K_{app}(\phi_0 - \phi')[FcS4]}$$
(2)

S4. Structural characterization of CPB and CPB NK-12

The TEM images (Figure S1) obtained from some sections of the TEM grid show the coexistence of cubic 3D-CsPbBr₃ and tetragonal 2D-CsPb₂Br₅, consistent with earlier reports.^{6–}



Figure S1. TEM images of CPB NK-12 (a-d) captured at different scales show some unusual, aggregated nanostructures resulting from ligand exchange.



Figure S2. (a) Histogram illustrating the DLS size distribution of CPB and CPB NK-12. The average size of the CPB and CPB NK-12 was calculated to be ~ 9 nm and ~ 149 nm, respectively. (b) Time-resolved PL profiles ($\lambda_{ex} = 375$ nm) of CPB ($\tau_{avg} = 5.84$ ns) and CPB NK-12 ($\tau_{avg} = 19.6$ ns) were monitored at 507 nm and 516 nm, respectively. After ligand exchange with NK-12, the average lifetime is improved by a factor of three.



Figure S3. (a) Comparative FTIR spectrum of CPB, CPB NK-12, and pure NK-12 highlighting the appearance of carbonyl stretch of amide (-NH-C=O) in CPB NK-12 after ligand exchange (b) ¹H NMR spectrum of CPB NK-12 in C_6D_6 . Starred (*) features are the solvent residual peaks appearing even after several washes.



S5. PL quenching control experiments for CPB and CPB NK-12 with FcS4

Figure S4. (a), (b) and (c) are the UV-vis absorption spectra, steady-state PL evolution, and Time-resolved PL spectra for CPB, respectively, with the sequential addition of FcS4. (d), (e) and (f) are the UV-vis absorption spectra, steady-state PL evolution, and Time-resolved PL spectra for CPB NK-12, respectively, with the sequential addition of FcS4. Time-resolved PL spectra were recorded using 375 nm pulsed excitation. A stable absorbance, significant emission quenching, and rapid decrease in PL lifetime of CPB NK-12 with increasing FcS4 concentrations indicated better charge transfer performance.

S6. The structural integrity of CPBNK-12 after quenching experiments



Figure S5. (a-c) TEM images of CPB NK-12 with FcS4 addition show the structural stability of the system with no significant change in the structural features.



Figure S6. Stability control. (a) Steady-state emission and (b) UV-vis absorption spectra of CPB NK-12 dispersed in toluene were acquired over a time interval of 2 hours. No substantial drop in intensity proved the stability of CPB NK-12 for the duration of FcS4 quenching experiments.

Table S1. Fitting parameters of the kinetic analysis of photoluminescence traces of CPB and CPB NK-12 (Figure S2b) with increasing concentration of FcS4 (Figure 3c, 3d, and Figure S4c, S4f).

[FcS4] (nM)	α ₁	f _{1(%)}	$ au_1$ (ns)	α2	f _{2 (%)}	τ_2 (ns)	α ₃	f _{3(%)}	τ_3 (ns)	$ au_{avg}$ (ns)
СРВ										
0	0.028	13.6	1.06	0.035	60.7	3.81	0.004	25.7	13.15	5.84
1.98	0.033	17.4	0.90	0.033	62.1	3.24	0.003	20.5	11.83	4.59
5.92	0.036	16.3	0.72	0.033	61.9	2.96	0.003	21.8	10.82	4.31
14.74	0.040	16.5	0.54	0.030	58.1	2.48	0.004	25.4	8.44	3.67
29.27	0.048	17.8	0.37	0.028	52.2	1.88	0.005	30.0	6.39	2.96
77.86	0.068	27.3	0.23	0.024	46.6	1.12	0.003	26.2	4.44	1.75
CPB NK-12										
0	0.022	3.6	0.95	0.023	21.5	5.39	0.017	74.8	24.62	19.6
1.98	0.030	7.4	0.88	0.027	33.6	4.52	0.011	59.0	19.86	13.3
5.92	0.040	13.4	0.74	0.025	41.9	3.59	0.006	44.7	16.61	9.03
14.74	0.055	24.6	0.52	0.020	42.4	2.5	0.003	33.0	13.33	5.59
29.27	0.064	29.3	0.37	0.019	41.3	1.73	0.002	29.4	9.52	3.62
77.86	0.086	38.9	0.22	0.016	37.9	1.14	0.002	23.2	6.81	2.10

The PL decay was fitted to a triexponential decay function (equation 3):

$$y = \alpha_1 e^{-\frac{t}{\tau_1}} + \alpha_2 e^{-\frac{t}{\tau_2}} + \alpha_3 e^{-\frac{t}{\tau_3}}$$
(3)

The average PL lifetime (τ_{avg}) can be determined using the following equation

$$\tau_{avg} = \frac{\sum_{i=1}^{3} \alpha_i \tau_i^2}{\sum_{i=1}^{3} \alpha_i \tau_i}$$
(4)

Alternatively, the pre-exponential factor, α_i and τ_i can be used to evaluate the fractional contribution (f_i), also defined as a relative integral contribution.

$$f_i = \frac{\alpha_i \tau_i}{\sum_i \alpha_i \tau_i} \tag{5}$$

Here, we calculated the average PL lifetime $(^{\tau}_{avg})$ of the triexponential decays as follows:

$$\tau_{avg} = f_1 \tau_1 + f_2 \tau_2 + f_3 \tau_3 \tag{6}$$

S7. Control experiment (dilution effect) for the PL quenching of CPB NK-12 on adding FcS4.



Figure S7. Comparative PL spectrum of CPB NK-12 on the addition of FcS4 (final concentration 77.86 nM) and equal volume (i.e., 35 μ L) of toluene to confirm the negligible effect of dilution in PL quenching of CPB NK-12.

S8. Determination of the number of FcS4 molecules per nanocrystal

We determined the number of acceptor molecules attached per NC using a previously reported model^{9,10} This model first assumes that the distribution of molecules on NC surfaces follows the Poisson distribution:

$$P(n) = \frac{e^{-m}m^n}{n!} \tag{7}$$

Where P(n) is the probability of finding n acceptor molecules per NC, and m is the average number of acceptor molecules attached to a nanocrystal.

The model also assumes that the adsorption of acceptors onto NC surfaces follows the Langmuir adsorption isotherm.

$$\theta = \frac{m}{N} = \theta_{max} \frac{K_a[A]}{1 + K_a[A]} \tag{8}$$

Where θ is the mean fractional surface coverage of acceptors on NC surfaces, N is the total number of available binding sites per NC, θ_{max} is the maximum fractional surface coverage of acceptors on NCs, K_a the binding constant of acceptors and [A] the total concentration of acceptors.

To estimate θ , the dependence of steady-state PL quenching on acceptor concentration was measured. With successive addition of acceptor molecules, the PL intensity decreased.

Now, the probability of finding NCs without any acceptor attached to it is given by the relative PL intensity in the presence of an acceptor $(^{I}/I_{0})$. The relationship between $^{I}/I_{0}$ and θ is given by the following equation¹¹

$$\frac{I}{I_0} = (1 - \theta)^N \tag{9}$$

Assuming that the acceptor, FcS4, preferentially binds to Pb^{2+} , N is calculated using the following equation:

$$N = \frac{\pi}{4} \left(\frac{6a^2}{\pi r_{pb^2}^2 +} \right)$$
(10)

Where *a* is the size of NCs and $r_{Pb^{2+}} = 0.119 \text{ nm}$. Using equation 9, the value of *N* for NCs was found to be ~ 8600. Finally, *m* values at each concentration of FcS4 are calculated using equation 7.



Figure S8. Plots for relative PL intensity and number of FcS4 molecules per nanocrystal with increasing concentration of Fcs4 for CPB and CPB NK-12.

Table S2. Estimated values of the average number of FcS4 molecules per NC, m corresponding to the total FcS4 concentration added.

FcS4 (nM)	m					
1 (11 (1)	СРВ	CPB NK-12				
0	0	0				
1.98	0.05	0.43				
3.95	0.10	0.77				
5.92	0.16	1.06				
7.89	0.23	1.31				
9.85	0.30	1.55				
14.74	0.44	1.90				
19.61	0.60	2.20				
24.45	0.75	2.47				
29.27	0.84	2.66				
48.73	1.26	3.16				
77.86	1.70	3.52				

S9. Decay kinetics analysis from transient absorption spectroscopy measurements

The bleach recovery kinetics obtained from transient absorption measurements were fitted to a bi-exponential and tri-exponential function for CPB and CPB NK-12, respectively (Table S3). The time constants τ_2 and τ_3 can be assigned to excitonic recombination and radiative recombination occurring in CPB and CPB NK-12. However, the shorter time constant (τ_1) observed in CPB NK-12 may correspond to the carrier trap states due to the occurrence of a dual phase after ligand exchange which corroborates well with the earlier report.¹²

[FcS4] (nM)	χ^2	$ au_1$ (ps)	$ au_2$ (ps)	$ au_3$ (ps)				
СРВ								
0	0.98	-	75 ± 5	1400 ± 100				
49.5	0.99	-	74 ± 3	1060 ± 80				
CPB NK-12								
0	0.95	2.50 ± 0.58	210 ± 30	2600 ± 600				
49.5	0.98	0.55 ± 0.03	86 ± 6	1300 ± 100				

Table S3. Fitting parameters for the transient absorption bleach recovery kinetics of CPB and CPB NK-12 with and without the addition of FcS4 in Figure (5a and 5b).

S10. Steady-state photolysis experiment for CPB NK-12 in the presence of FcS4.

According to our previous study,¹³ FcS4 molecules possess a low molar extinction coefficient, leading to very low absorption at our experimental conditions (concentration ~ 49.5 nM). This is why we have not observed any significant features for FcS4 and oxidized FcS4 in the transient absorption spectrum. Further, considering the strong attraction and efficient PL quenching (of CPB NK-12) in the presence of FcS4, we attempted a steady-state photolysis experiment for CPB NK-12 (12.9 nM) by increasing the FcS4 concentration to 100 μ M. However, due to the dominant extinction of CPB NK-12, we have plotted the difference absorption spectrum at different times of visible light exposure to observe the distinct change. A significant increase in the absorbance in the 600 -700 nm range could be assigned to the oxidized FcS4.^{13,14}



Figure S9. Steady-state photolysis of CPB NK-12 in the presence of FcS4. (a) the difference absorption spectrum of CPB NK-12 with FcS4 (~100 μ M) on exposure to visible light. The appearance of a hump-like feature that increased with time (highlighted with green background) corresponds to the oxidized FcS4. (b) difference spectrum for the control experiment performed in the dark, keeping the other experimental parameters constant (c) difference spectrum for the control experiment performed in the control experiment performed in the absence of CPB NK-12, i.e., only FcS4. The absence of any significant feature in (b) and (c) shows the feasibility of hole transfer from CPB NK-12 to FcS4, which follows other spectroscopic results featuring hole transfer dynamics.

S11. Estimation of photoluminescence quantum yield (PLQY).

PLQY of CPB NCs before and after NK-12 treatment was estimated by the relative quantum yield method following equation 11:

$$\Phi_s = \Phi_r \times \frac{A_r}{A_s} \times \frac{I_s}{I_r} \times \left(\frac{\eta_s}{\eta_r}\right)^2 \tag{11}$$

where Φ , A, I, and η represent the PLQY, absorbance at the excitation wavelength ($\lambda_{ex} = 365$ nm), integrated PL intensity, and refractive index of the solvent, respectively. The subscripts s and r symbolize sample and reference. As reported earlier, we used coumarin-152A dye (in acetonitrile solvent) as the reference standard with a PLQY of 22%.¹⁵ Refractive index values

for toluene (η_s) and acetonitrile (η_r) used were 1.497 and 1.344, respectively. Using this method, PLQY is estimated to be 25 % for CPB and 24% for CPB NK-12 NCs.



Figure S10. Estimation of relative PLQY. Absorption and PL spectra of (a) coumarin 152-A dye recorded in acetonitrile, (b) CPB and CPB NK-12 recorded in toluene. PL spectra were recorded at the excitation wavelength, $\lambda_{ex} = 365$ nm.

S12. X-Ray Photoelectron Spectroscopy (XPS) analysis.



Figure S11. (a) XPS survey scan of CPB and CPB NK-12. (b), (c) and (d) Comparative high-resolution XPS spectra of N 1s, Pb 4f, and Br 3d, respectively, for CPB and CPB NK-12.

After NK-12 treatment (Figure S11a), the overall survey spectra of CPB exhibit stronger peaks for Pb 4f, Br 3d, and N 1s, which are relatively weak in CPB. The well-resolved -NH₃⁺ (401.65 eV) and -NH₂ (399.74 eV) peaks in N 1s core level spectra of CPB NK-12 reveal an effective ligand exchange of native OAm/OAc ligands by NK-12 ligand. A slight decrease in the binding energy of Pb 4f and Br 3d from CPB to CPB NK-12 (Figure S11c, S11d) could be attributed to the NK-12 ligand-induced structural changes forming dual phase CPB/CP₂B₅ nanostructures, which corroborates with the earlier report.¹⁶



Figure S12. XPS analysis of CPB NK-12 before and after FcS4 addition. (a) XPS survey scan of CPB NK-12 and CPB NK-12+FcS4 sample. (b), (c) and (d) Comparative high-resolution XPS spectra of N 1s, Pb 4f, and Br 3d, respectively, for CPB NK-12 before and after adding FcS4.

Figure S12b shows a small increase in the binding energies of $-NH_3^+$ (401.82 eV) and $-NH_2$ (399.91 eV) peaks in the high-resolution N 1s spectra after FcS4 addition to CPB NK-12. While the binding energies of Pb 4f and Br 3d peaks are slightly decreased, as seen in Figure S12c and S12d, respectively. This supports our hypothesis that the improved FcS4 binding with CPB NK-12 is owing to the coulombic attraction between the positively charged NK-12 ligand attached to the NC surface and the FcS4 molecule with -COOH functional group.

REFERENCES

- L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X.
 Yang, A. Walsh and M. V. Kovalenko, *Nano Lett.*, 2015, 15, 3692–3696.
- 2 J. De Roo, M. Ibáñez, P. Geiregat, G. Nedelcu, W. Walravens, J. Maes, J. C. Martins, I.
 Van Driessche, M. V. Kovalenko and Z. Hens, *ACS Nano*, 2016, **10**, 2071–2081.
- 3 C. K. Ng, W. Yin, H. Li and J. J. Jasieniak, Nanoscale, 2020, 12, 4859–4867.
- 4 H. A. Benesi and J. H. Hildebrand, J. Am. Chem. Soc., 1949, 71, 2703–2707.
- 5 S. N. Sharma, Z. S. Pillai and P. V. Kamat, J. Phys. Chem. B, 2003, 107, 10088–10093.
- 6 C. Qin, T. Matsushima, A. S. D. Sandanayaka, Y. Tsuchiya and C. Adachi, J. Phys. Chem. Lett., 2017, 8, 5415–5421.
- 7 L. Ding, B. Borjigin, Y. Li, X. Yang, X. Wang and H. Li, ACS Appl. Mater. Interfaces, 2021, 13, 51161–51173.
- 8 J. Li, H. Zhang, S. Wang, D. Long, M. Li, Y. Guo, Z. Zhong, K. Wu, D. Wang and T. Zhang, *RSC Adv.*, 2017, 7, 54002–54007.
- 9 K. Wu, G. Liang, Q. Shang, Y. Ren, D. Kong and T. Lian, J. Am. Chem. Soc., 2015, 137, 12792–12795.
- 10S. Sarkar, V. K. Ravi, S. Banerjee, G. R. Yettapu, G. B. Markad, A. Nag and P. Mandal, *Nano Lett.*, 2017, **17**, 5402–5407.
- 11 A. J. Morris-Cohen, V. Vasilenko, V. A. Amin, M. G. Reuter and E. A. Weiss, ACS Nano, 2012, 6, 557–565.
- 12Z.-P. Huang, B. Ma, H. Wang, N. Li, R.-T. Liu, Z.-Q. Zhang, X.-D. Zhang, J.-H. Zhao, P.-Z. Zheng, Q. Wang and H.-L. Zhang, J. Phys. Chem. Lett., 2020, 11, 6007–6015.
- 13S. Singh, D. Mittal, V. Gurunarayanan, A. Sahu, R. Ramapanicker and V. G. Rao, *Journal of Materials Chemistry A*, 2022, **10**, 21112–21123.
- 14 V. Gurunarayanan and R. Ramapanicker, Journal of Peptide Science, 2021, 27, e3332.
- 15 A. K. Satpati, M. Kumbhakar, S. Nath and H. Pal, *Photochemistry and Photobiology*, 2009, **85**, 119–129.
- 16S. K. Balakrishnan and P. V. Kamat, Chem. Mater., 2018, 30, 74-78.